A PETROLOGICAL STUDY OF THE NANDEWAR VOLCANO

By

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This thesis is the result of research work carried by the author (undersigned) from 1962 to 1965. All the work contained in this thesis, with the exceptions listed below, is the result of the author's own work and has not previously been published.

Some of the chemical determinations have been checked by the author's supervisor, Dr. A.J.R. White, and some of the X-ray fluorescent spectrograph values have been checked and duplicated by Dr. White, Mr. B.W. Chappell and Mr. J. Pennington. Mrs. J. Morgan determined several FeO values in some of the rocks and minerals. Mr. A.J. Easton determined some of the oxides in the cossyrite, where micro-analytical methods were required.

The U, Th and K values derived from gamma ray spectrometric measurements were determined by Dr. K.S. Heier, who also calculated the Th/U, Th/K and U/K ratios. The conclusions drawn from these measurements are solely those of the present author, who accepts responsibility for them. The measurements will be the subject of a subsequent communication by Dr. Heier and and the author.

Much assistance and instruction was given to the author by various members of the Geology Department, and this help has been detailed in the acknowledgements.

All the conclusions drawn from the data are the author's own.

Signed .....M. J. Abbott.....

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ABSTRACT

The Nandewar alkaline volcano lies to the west of the New England Tableland, on the western margin of the Border Thrusts which separate the eastern folded and faulted rocks from the relatively undisturbed rocks to the west and which localised the later volcanism.

The basement of the volcanic complex consists of orogenically folded Carboniferous rocks, separated by the Border Thrusts from flat-lying Permian Lower Coal Measures overlain by Triassic rocks.

The mountains proper are the remains of a Tertiary alkaline volcano which consisted of a braod basaltic shield with well-defined flows dipping away from the centre. Basaltic and trachyandesitic flows form most the volcanic pile now exposed, but some of the youngest coulees are trachytic. The volcano is now a mature erosional caldera.

Within the caldera dykes, stocks, plugs, sills and domes of trachyte intrude the deformed country rocks and the remnants of the basaltic shield. The trachytes represent the waning stages of ac activity.

Sills of teschenite intrude both Permian and Mesozoic sediments and these show the same differentiation trends as the Black Jack Gunnedah sill. A very fine grained chilled contact teschenite is more basic than the Black Jack contact rocks.

A sill of analcitite intrudes Permian sediments near Bullawa creek, and at least 60 per cent of the sill consists of ultrabasic xenoliths and xenocrysts. An analysed diopside xenocryst initially formed under granulite facies conditions, and a phlogopitic biotite formed in a high temperature, ultrabasic environment. The analcitite matrix consists of titanaugite set in a base of analcite, nepheline and felspar.

The teschenites and analcitite are strongly undersaturated, in contrast to the later basalt and trachyandesite extrusive rocks.

The basaltic shield of the volcano consists of a large number of flows, with very little sign of explosive activity. The bulk of the flows are trachyandesites, and olivine basalts and basalts are subordinate. Three groups of basaltic rocks exist: porphyritic olivine basalts, 'big felspar' basalts and trachyandesites.

The 'big felspar' basalts are very distinctive in hand specimen because of the abundant plagioclase phenocrysts. The trachyandesites are usually nonporphyritic, although microphenocrysts of plagioclase can appear.

The porphyritic olivine basalts consist of phenocrysts of olivine, titanaugite and plagioclase, set in a groundmass of plagioclase, clinopyroxenes and magnetites. The 'big felspar' basalts consist of large plagioclase phenocrysts set in a groundmass of clinopyroxenes, plagioclases and magnetites. The trachyandesites consist of small laths of plagioclase, together with augites and magnetites, with a trachytic flow structure. The presence of potash oligoclase and calcic anorthoclase is suspected in these rocks.

The trachytes have been divided into the two felspar types (plagioclase + alkali felspar) and one felspar types (alkali felspar alone). The two felspar trachytes possess two successive members of the felspar fractionation sequence, a potash oligoclase and calcic anorthoclase, whereas the one felspar trachytes and comendites have one felspar of the minimum melting composition $Ab_{65}Or_{35}$.

Two felspar trachytes have phenocrysts of oligoclase and anorthoclase, both zoned and rimmed with alkali felspar, and albites and felspar laths, pale green augite crystals, titanomagnetites and pseudomorphs after olivine in the groundmass. Stumpy and rhomboidal felspars are typical in these rocks.

The one felspar trachytes have sanidine - anorthoclase phenocrysts set in a groundmass of felspar laths of the same composition ($Ab_{65}Or_{35}$). The ferromagnesian minerals are hedenbergite (as phenocrysts), or aegerine-augite (as interstitial groundmass constituents), cossyrite, and riebeckite-arfvedsonite, together with some magnetite. Katophoritic amphibole has been detected.

In the comendites, only alkali felspar and quartz are present. These rocks are usually porphyritic.

The olivines, which are quite scarce in the alkaline rocks are relatively iron-rich, but do not persist beyond the middle stage of differentiation.

The pyroxenes are present in all the rocks except the comendites. The trend shown by the clinopyroxenes from the basalts and trachytes is from diopsidic augites straight across the Di-He-En-Fs quadrilateral parallel to the Di-He join towards hedenbergite. Only in the latest stages of differentiation, in the interstitial aegerine-augites, does $NaFe^{3+}$ enrichment occur, and a final composition of $He_{50}Ac_{50}$ occurs. Low partial pressures of oxygen until the latest stages are indicated.

Cossyrite is common in some of the trachytes, and it has large amounts of ferrous iron. The conditions leading to the appearance of

cossyrite are: peralkalinity, low partial pressures of oxygen, and concentration of TiO_2.

Titanomagnetites are common in all the alkaline rocks except the comendites. There is little enrichment in $FeTiO_3$ in the basalts and trachyandesites, but in the two felspar trachytesenrichment in the $FeTiO_3$ component is indicated by exsolution lamellae of ilmenite and by the unit-cell dimensions. The titanomagnetites from the cossyrite trachytes approach pure magnetite. The absence of hematite indicates moderate to low partial pressures of oxygen.

The felspars are the most abundant minerals in the alkaline series, and range from plagioclases (An_{65}) in the basalts, through andesines and potash oligoclases in the two felspar trachytes, calcic anorthoclases together with minor potash oligoclase in the two felspar trachytes, to alkali felspars of compositions approaching $Ab_{65}Or_{35}$ in the one felspar trachytes and comendites. High temperature optics are present in the plagioclase phenocrysts from the basalts, and low temperature optics for the groundmass plagioclase from the trachyandesites. The alkali felspars approach the sanidine-anorthoclase series, and have little exsolution. The sodic anorthoclases have cross-hatched twinning.

The trace elements Sr, Rb, Ba, Zr, U and Th have been determined. The Rb content rises with differentiation, while the K/Rb ratio falls. The Sr and Ba are both rapidly depleted with differentiation, and these two elements show co-variance. Zr rises steadily throughout the sequence, as do both U and Th, which enter the zircons.

Even the most basic olivine basalt is relatively differentiated, and the MgO is low in the basalts. The SiO_2 rises to quite high

values in the late differentiates; the Al_2O_3 falls in the comendites; the total iron falls in the trachytes and comendites after being steady in the basalts and trachyandesites; the Fe_2O_3 and FeO also fall in the trachytes and comendites (although the FeO is higher in the cossyrite trachytes); the CaO and MgO fall steadily throughout the sequence; the Na_2O and K_2O rise until quite a late stage, and then fall quite sharply in the comendites. The calc-alkaline andesites have higher MgO, and CaO and lower Na_2O and K_2O, and higher normative Q, an and en and lower or than alkaline rocks of equivalent silica content.

The alkaline series shows little absolute iron enrichment, but does have a very strong enrichment in alkalies, the iron and magnesium being almost nil in the comendites. There is no preferential enrichment in either K or Na in the late stages. The final compositions approach the minimum melting composition in the system SiO_2-$NaAlSi_3O_8$-$KAlSi_3O_8$, and are thus regarded as the result of fractionation.

The rocks become peralkaline once the cossyrite trachyte stage of differentiation is reached. These trachytes have higher peralkalinity ratios than the comendites.

All the alkaline rocks are saturated or oversaturated, and high normative hy in the basalts is accounted for by oxidation and alteration of the rocks. The cossyrite trachytes have high Fe^{2+}/Fe^{2+} + Mg ratios in the ferromagnesian minerals in the norm, while in the comendites nearly all the iron is ferric.

The 'big felspar' basalts, with 70 per cent plagioclase phenocrysts, are assumed to have been quite abundant in the subjacent magma chamber. Withdrawal of large amounts of An from the magma results in a peralkaline

derivative.

All the evidence points to the development of the whole alkaline series in the Nandewars by differentiation from an alkali olivine basalt parent magma. This magma is distinct from the type yielding the strongly undersaturated teschenites and analcitites.

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INTRODUCTION

GENERAL SETTING OF EASTERN AUSTRALIAN TERTIARY ALKALINE VOLCANIC ROCKS.

The general geological evolution of Eastern Australia has been reviewed by Voisey (1959a, and 1959b).

The general picture is of a stable continental cratonic block in the west, flanked to the east by successive mobile belts of island arcs and volcanoes, which are welded onto the stable continental cratonic block in orogenies which have occurred from the Silurian to the Permian, the eastern margin of the Australian continent being essentially stable since that time (Voisey, 1959b).

Since the Mesozoic, there have been extensive outflows and intrusions of alkaline and subalkaline magmas throughout Eastern Australia.

In Victoria there are widespread lava flows, and Edwards (1935, 1938a, 1938b) has divided these lavas into two series - the Older Series (Oligocene to Miocene) and the Newer Series (Pliocene to Recent). The Older volcanic series consist of crinanites, olivine titanaugite dolerites, olivine titanaugite basalts, olivine basalts, olivine nephelinites, limburgites, monchiquites, camptonites, tinguaites and phonolites. This series is alkaline, and strongly undersaturated, and is also strongly eroded, occurring mostly to the south and east of Melbourne.

The Newer volcanic series, much less eroded, extend north-west and west from Melbourne as a broad plain 10,000 square miles in extent. Some cones and necks are preserved, but most of the lavas are now seen as flow residuals. Edwards (1938a) has recognised in the Newer series limburgites, olivine-labradorite, olivine-andesine and olivine-oligoclase basalts, oligoclase basalts, trachybasalts, olivine-anorthoclase trachytes,

anorthoclase-olivine trachytes, trachyphonolites, trachyandesites, and solvsbergites.

The region of the volcanic rocks in Victoria has been stable since the Devonian.

In south-eastern Queensland, quite a minor proportion of the lavas are alkaline, according to Richards (1916). Most types appear to be sub-alkaline. However anorthoclase-aegerine-riebeckite-arfvedsonite trachytes occur, as well as trachyandesites grading into labradorite basalts. The basalts are most abundant, being poured out as flows which have formed a basaltic shield volcano in the MacPherson Ranges, which straddle the N.S.W. - Qld. border. Trachytes intrude this eroded basaltic shield (for example, Mt. Warning). Some of the basalts appear to be quite alkaline in type and mugearites have been detected.

Richards (1916) holds that these volcanic rocks are early Tertiary, or at least Post-Walloon (Triassic-Jurassic). Three divisions of lavas exist with a total thickness of about 3,000 feet. Most of the lower sequence is basaltic, the middle sequence is mostly rhyolitic and trachytic, and the upper sequence, which has the largest bulk of the three, is basaltic and andesitic. The middle sequence and to some extent the lower sequence are characterised by abundant pyroclastic material.

Jensen (1906) has described alkaline pantellerites and comendites from the Glass House Mountains, to the north of Brisbane, Qld. These rocks occur as steep-sided plugs and necks intruding sedimentary basement rocks. Trachytes also occur in the Glass House Mountains.

The closest Tertiary alkaline volcano to the Nandewars in the Warrumbungle Mountains, about 100 miles to the south-west. The

physiography of this volcano is very similar to the Nandewar volcano, with the appearance of trachytic domes and plugs intruding an eroded basaltic shield volcano.

Jensen (1907a) has studied the Warrumbungle Mountain volcanic rocks and has found the following types (op. cit., p. 587):

"(a) Arfvedsonite trachytes, comendites and pantellerites, light grey or bluish in colour.

(b) Dark aegerine trachytes, phonolitic trachytes and phonolites.

(c) Trachydolerites.

(d) Andesitic rocks and basalts."

Undersaturated rocks such as nosean-phonolites and nosean-leucitophyres have been detected.

The present author has had the opportunity of examining the nosean-phonolites and nosean-leucitophyres studied by Jensen (1907a), these samples being the same as those formerly collected by Jensen. No sign of nosean or leucite could be detected, and Joplin (1964, p. 84) states: "Jensen has described leucite and nosean-bearing trachytes in the Warrumbungle Mountains, but re-examination has not confirmed his identifications."

Phonolites have, however, been found in the Warrumbungles, and in this respect the trachytic rocks in the Warrumbungles are different from those in the Nandewars in being undersaturated rather than oversaturated with silica.

The presence of trachytic tuffs and breccias in the Warrumbungles (Jensen, op. cit.) has not been duplicated in the Nandewars, and trachyte plugs appear to be more abundant in the Warrumbungles.

The widespread undersaturated alkaline rocks in the New England area of N.S.W. (including the teschenite sills near Gunnedah, typified by the Black Jack sill (Wilkinson, 1958), and the undersaturated analcite basalts near Glen Innes at Spring Mountain (Wilkinson, 1962)) show similarities to the teschenites and analcitites in the Nandewar Mountains area, but are quite distinct from the mountain-building alkaline volcanics which represent a later and separate phase of volcanic activity.

GENERAL DESCRIPTION OF THE NANDEWAR VOLCANIC ROCKS

The Nandewar Mountains cover an area of approximately 400 square miles, and are situated about 20 miles east of Narrabri, a town 350 miles north-west from Sydney, New South Wales.

The region lies to the west of the New England Tableland, and the mountains lie on the western margin of the Border Thrust structural region as defined by Voisey (1959a) in his study of the tectonics of north-eastern New South Wales. The Border Thrusts "separate the region of intense folding and faulting from the relatively undisturbed areas to the west" (Voisey, op. cit., p. 194). The Border Thrusts were formed in the Permian, when the orogeny deforming the New England geosynclien began. The region of the Thrust(s) appears to be the line of weakness which localised later volcanism.

The basement of the volcanic complex is described in the section on the basement rocks.

The mountains proper are the remains of a Tertiary alkaline volcano consisting of a basaltic shield with well defined flows dipping away from the centre. On the Kaputar Plateau, the southern flank of the volcano, the flows dip south at about 10°, while on Castle Top Mountain, about 10

miles to the north-west, the flows dip north-west at about 5°. These flows originally formed part of a broad basaltic dome. Basaltic and trachyandesitic flows form most of the volcanic pile now exposed, but some of the youngest coulees are trachytic. The volcano is now seen as a mature erosional caldera (in the sense of Cotton, 1952, p. 384 et. seq.), with the original centre of the volcano eroded away.

Within the caldera, between Bullawa Creek and Killarney Gap, dykes, stocks, plugs, sills and dome shaped masses of trachyte are intruded into the deformed country rocks. Dykes and plugs of trachyte also intrude the remnants of the basaltic shield, so some of the trachytes are younger than the basaltic rocks. The trachytes appear to represent the waning stages of activity, but the possibility that some of the trachytes may precede the basaltic and trachyandesitic shield-building activity has been considered. If the assumption is made that the order of extrusion was in the order of increasing differentiation (on petrogenetic grounds a reasonable assumption) then the possibility of trachytes preceding the basaltic rocks in the time sequence must be ruled out.

Previous Work

Little previous work has been done in the Nandewar province on the geology.

Jensen (1907) was the first to publish on the geology of the area. He mapped the area in broad outline, his most detailed mapping being in the region of Bullawa Creek. Elsewhere, his mapping is only on a very general basis. Petrographical descriptions of the rocks are also included, and he recognised: alkaline rhyolites, alkaline trachytes, phonolites,

alkaline andesites, alkali basalts, calcic rhyolites and basalts, together with alkaline syenite porphyries, felspathoid rocks - pulaskite porphyries, augite porphyries and teschenites, and bronzite peridotite porphyries (monchiquite lamprophyre).

Jensen also carried out 10 analyses of the alkaline rocks, ranging from the trachytes to the basalts, and these are set out in Tables 1-4. Some of the analyses are of doubtful accuracy; in two cases the totals are over 101 per cent, and the analysis of the phonolitic trachyte (6) has a high Al_2O_3 and that of the dolerite (8) has a low value for Al_2O_3. The norm calculation carried out by Jensen for the trachyte from Mt. Ningadhun (1) shows that there is 5.5 per cent normative corundum, and the Al_2O_3 or Na_2O and K_2O values appear to be in error. Furthermore, the dolerite analysed by Jensen (8) would now be called a teschenite, and there is no normative ne. Thus the analyses of Jensen must be used with caution. The analysis of the monchiquite lamprophyre (9) is an analysis of the analcitite (described in this thesis) together with all the ultrabasic xenoliths, and this analysis is thus of little value. Bearing all these reservations in mind, it is still possible to use the data of Jensen (1907) for comparative purposes, and the chemical analyses will be discussed in the section of this thesis on the chemistry of the alkaline rocks.

Hanlon (1948a) also carried out a geological reconnaissance of the area as part of the mapping program in the North-Western Coalfield of New South Wales. He paid most attention to the Permian and Triassic sediments, delineating their outcrop, and their relations to the overlying

volcanic rocks. Apart from mapping the limits of outcrop of the alkaline rocks, and their contact with the sediments, no attention was paid to them.

McKelvey and White (1964) have produced a map (1:100,000 scale) of the Horton map sheet, with marginal notes on the rocks. Those part of this text which relate to the volcanic rocks were written in consultation with the author of the present thesis. Much the same comment with regard to the attention of these workers to the volcanic rocks can be made as for Hanlon's (1948a) work, but McKelvey and White have been mainly concerned with the Carboniferous and Devonian sediments to the east of the Nandewar Mountains proper. In the map of the volcanic area produced by the present author, use has been made of the information of McKelvey and White (1964) with regard to the sediment - volcanic rock contacts. Unpublished information collected by White and McKelvey on the geology of the Tareela map sheet (shortly to be published in the same series and on the same scale as the Horton sheet) has also been used in compiling the map in this thesis.

No other work has been done on the geology of the volcanic rocks of the Nandewar Mountains.

Johnson (1961) has worked on the area of the lava flows on the Kaputar Plateau.

JOHNSON, I.R., 1961, Geology of the South-Western portion of the Nandewar Mountains: Unpubl. B.Sc. Hons. Thesis, Univ. New England.

TABLE 1

CHEMICAL ANALYSES OF ROCKS IN THE NANDEWARS BY JENSEN (1907)

	1	2	3	4	5
SiO_2	64.63	64.31	64.38	58.90	61.27
TiO_2	0.58	1.25	0.56	1.47	1.02
Al_2O_3	16.55	15.05	17.13	16.48	16.00
Fe_2O_3	2.93	3.39	5.62	2.98	2.59
FeO	1.16	2.33	0.28	3.35	4.04
MnO	0.08	0.09	0.00	0.08	0.10
NiO	tr	0.03	0.00	0.05	tr
MgO	0.16	0.14	0.03	0.78	0.39
CaO	0.46	1.54	0.61	2.78	1.93
Na_2O	5.23	4.77	4.59	4.09	4.25
K_2O	6.11	6.59	6.49	6.05	6.31
H_2O^+	1.05	0.79		0.82	0.64
H_2O^-	1.35	0.39		0.34	0.36
CO_2	tr	0.00	1.63	1.50	0.16
ZrO_2	0.07	0.09			
Cl	tr	0.02			
F		0.10			
less O=F		0.05			
Total	100.36	100.93	101.32	99.67	99.06

1. Trachyte, Mt. Ningadhun.
2. Trachyte, Mt. Deriah.
3. Trachyte, near Dripping Rock.
4. Pulaskite porphyry, branch of Oakey Creek, near Mt. Odin.
5. Phonolite, Oakey Creek.

TABLE 2

CHEMICAL ANALYSES OF ROCKS IN THE NANDEWARS BY JENSEN (1907)

	6	7	8	9	10
SiO_2	51.98	51.30	47.20	36.88	56.63
TiO_2	4.71	2.78	4.31	2.10	2.00
Al_2O_3	22.46	16.13	11.78	4.53	17.71
Fe_2O_3	2.48	3.01	1.94	2.03	3.61
FeO	1.87	6.92	9.04	9.67	4.64
MnO	0.08	0.19	0.26	0.04	0.03
NiO	0.04	0.05	0.03	0.07	0.00
MgO	0.83	2.58	9.95	25.40	1.47
CaO	4.63	6.97	11.63	7.61	4.06
Na_2O	3.66	4.00	1.61	1.17	5.11
K_2O	3.93	2.07	1.67	0.43	3.65
H_2O^+	1.08	1.89	1.24	0.82	0.70
H_2O^-	2.06	0.50	0.28	0.58	0.49
CO_2	0.04	1.64	0.17	8.10	0.01
ZrO_2				0.06	0.06
$S(FeS_2)$				0.17	
less O=S				0.08	
Total	99.85	100.03	101.11	99.58	100.17

6. Phonolitic trachyte, Mt. Ningadhun.
7. Labradorite porphyry, branch of Oakey Creek near Mt. Odin.
8. Dolerite, laccolite, Dongo Creek.
9. Monchiquite lamprophyre, sill, Dingo Creek.
10. Akerite, head of Oakey Creek and Bullawa Creek.

TABLE 3

NORMS OF THE NANDEWAR ROCKS CALCULATED BY JENSEN (1907) SPECIMEN NUMBERS AS IN TABLE 1 .

	1	2	3	4	5
Q	9.48	9.84	11.70	8.46	7.26
or	36.14	38.92	38.36	35.58	37.25
ab	44.02	40.35	38.78	34.58	35.63
an	2.50		1.95	4.45	6.12
C	5.50		1.84	1.63	
zr	0.18	0.18			
di		0.90			1.89
wo		2.09			
hy	0.53		0.10	3.22	3.70
ol					
mt	2.32	3.94		4.41	3.71
il	1.06	2.28	0.46	2.89	1.98
hm	1.28	0.64	5.70		
cc				3.40	0.40
sph			0.78		
H_2O	2.40	1.18	1.63	1.16	1.00
Total	100.43	100.32	101.30	99.78	98.94

TABLE 4

NORMS OF THE NANDEWAR ROCKS CALCULATED BY JENSEN (1907) SPECIMEN NUMBERS AS IN TABLE 2 .

	6	7	8	9	10
Q	6.36	3.54			2.76
or	22.80	12.23	11.68	2.22	21.13
ab	31.44	34.58	13.62	9.96	42.97
an	13.62	19.46	19.18	5.84	15.01
C	7.24				
di		4.08	29.42		3.56
hy	2.36	10.45	1.73	21.86	3.95
ol			12.46	33.96	
mt		4.41	2.78	5.88	5.34
il	3.95	5.17	8.06	3.95	3.80
hm	2.56				
cc		3.70	0.30		
sph	6.47				
ms				3.02	
H_2O	3.14	2.39	1.52	1.40	1.19
Total	99.94	100.01	100.75	99.59	99.71

BASEMENT ROCKS

THE BASEMENT ROCKS

The geology of the basement rocks is more fully treated in an earlier thesis by the author (Abbott, 1961).

To the east, the basement rocks consist of folded and faulted Carboniferous conglomerates and arenites with a large pyroclastic contribution, welded and vitric tuffs, some of which are probably ignimbrites, and varve shales.

To the west the basement rocks consist of relatively flat-lying Permian rocks believed to be Lower Coal Measures (Hanlon, 1948 b.) The sequence consists of a series of shales with abundant plant fossils and some coal. Some andesite flows are also found in the Permian sequence.

The gently dipping, completely unfolded Triassic sandstone sequence overlaps the Permian and has very uniform lithology. The Triassic also rests on the Carboniferous in the east, in places with a large angular unconformity.

A series of teschenite sills and sill-like masses intrude both the Permian and Triassic. The teschenites show great similarity to the Black Jack sill further to the south (Wilkinson, 1958). The intrusion of the teschenite is not believed to be connected with the later oversaturated alkaline volcanism in the main Nandewar phase.

The Carboniferous sequence to the east is separated by a major structural discontinuity from the flat-lying Permian and Triassic rocks to the west. Voisey (1959) proposed that this discontinuity, called by him a "Border Thrust" of the New England geosyncline, undergoing

orogenesis in the Permian, was a major overthrust fault.

CARBONIFEROUS

Benson (1913) named the rocks of the area the Rocky Creek conglomerates, stating that the series consisted of interbedded conglomerates with volcanic pebbles and acid lavas. He dated the beds as Lower Carboniferous, suggesting a thickness of 2,000 feet for the sequence.

Hanlon (1948b) correlated the Rocky Creek conglomerates with the Upper Kuttung, the correlation being reinforced by the presence of varvoid sediments and some true varves overlying the Rocky Creek conglomerates, these being Upper Carboniferous.

Suggested correlation, (Hanlon, 1948b):

Permian	
Carboniferous	
Kuttung Group:	Varves and varvoid sediments, glacial and fluvioglacial rocks. Rocky Creek conglomerates, acid tuffs and volcanic rocks.

The conglomerates are in places very coarse, pebbles being up to 2 feet in size. They are interbedded with both gritty and sandy beds of the same composition and acid volcanic tuffs with vitroclastic texture.

The arenites have poorly sorted angular fragments with a predominance of labile constituents. All the arenites have the features of

terrestrial outwash and lacustrine deposits, and fluvioglacial sediments. The great variety of lithic fragments is typical of these rocks, and mineral fragments are also varied. Andesite pebbles, granite and aplite pebbles, shale pebbles, vitric welded dacitic and rhyolitic tuff pebbles, biotite flakes, quartz fragments, plagioclase fragments, alkali felspars, magnetites and opaque iron oxides, amphibole fragments, zircons and apatites have been recognised. The cement is dominantly chloritic, but limonitic cement has been found in places. Zeolites are present, particularly in the cement, as a result of burial metamorphism.

The volcanic rocks in the Upper Kuttung are all acid, glassy, and show well developed vitroclastic texture. Almost all have phenocrysts either of quartz, albite-oligoclase, sanidine, or of albite alone. Most of the volcanic rocks are now devitrified and conctain zeolites.

Fine grained varvoid sediments have also been found in the Carboniferous. They consist of alternating bands of fine and coarse quartz fragments set in a limonite matrix. Some dropped pebbles are present. It has been suggested that these varvoid sediments represent volcanic ash deposits (Coombs, 1958).

The Carboniferous basement rocks in the Upper Rocky Creek area are either the products of shallow water deposits formed by the erosion of a dominantly volcanic terain (the conglomerates and arenites), or the results of explosive volcanic outbursts, presumably in nuees ardentes (the welded tuffs and ash flows), or deposits from frigid conditions (the varve shales and varvoid sediments).

PERMIAN

The Permian sequence is faulted but unfolded. The sequence is further disturbed in places by the intrusion of teschenite.

The Permian rocks outcrop on the eastern slopes of Killarney Gap above and below the teschenite, and also in the Upper Bullawa Creek area. Hanlon's (1948b) subdivision of the Permian will be followed:

Permian: Upper Marine Series, Barra Group

Lower Coal Measures, Nandewar Group

Hanlon (op. cit. p. 303) states "The coal bearing strata in the Narrabri district have always been regarded as belonging to the Upper Coal Measures. It now appears that they form part of the Lower Coal Measures and that the Upper Coal Measures are missing, being overlapped by the Triassic, which rests directly on Upper Marine beds. In the northern and eastern parts of the district (Killarney Gap area) the Upper marine seems to be overlapped in turn, and it is likely, at least to the north, that the Triassic beds rest directly on Lower Coal Measures. Lower Marine beds do not outcrop in the area and it is unlikely that lavas of this age, found further south, are developed. However, if they are developed, the lack of outcrops could easily be explained as being due to the elimination by faulting which occurs in the area".

The Permian sequence in the Nandewar Mountains area consists of sandstones with ironstone concretions, shales with plant fossils, and a few thin coal bands. In the sequence along Bullawa Creek the following plant fossils have been identified:

Noeggerathiopsis sp.
Glossopteris sp.

The Permian sequences both on the slopes of Killarney Gap and in Bullawa and Dingo creeks have dips up to 30°S.E.

Several andesite flows occur in the Permian sequence in both the upper reaches of Bobbiwaa Creek and Bullawa Creek.

The Bullawa Creek andesites occur below the teschenites. They consist of small laths of plagioclase together with abundant small magnetites and pyroxenes, some of which are possibly hypersthenes. Two chemical analyses of these andesites have been made (Table No. 35). They have high normative anorthite, quartz, and hypersthene, features which, together with the modal presence of hypersthene in the groundmass of the lavas, suggests calc-alkaline character.

The Bobbiwaa creek andesites have fine grainsize and consist of plagioclase laths (An_{20-67}; mostly andesine) in trachytic flow structure, hypersthene, and some magnetite.

The presence of these lavas suggests that they can be correlated with the Lower Marine lavas further south (Manser, 1960), contrary to the findings of Hanlon (1948b).

MESOZOIC (TRIASSIC)

The sequence, believed by Hanlon (1948b) to be Triassic overlapped by the Jurassic in places, consists of well washed quartzose sandstones, with basal conglomerates and shale layers.

The conglomerates have rounded jasperoid pebbles, and also pebbles

of acid volcanics, while both the sandstones and conglomerates have a clayey matrix. The sequence passes rapidly up into uniform sandstone after about 25 to 50 feet of alternating sandstone, shale and conglomerate.

The Triassic rests on the Permian with a slight unconformity. The nature of the contact of the two series of rocks is that of progressive overlap of the Triassic rocks upon the Permian (Hanlon, 1948b). The Triassic also outcrops above some of the Carboniferous rocks to east with a large angular unconformity. The Triassic sequence has a regional dip of from 5° to 10° south-west, and the teschenite sills generally intrude this sequence. The greatest extent of the Triassic rocks is seen in the west of the Nandewars, the Triassic capping the Carboniferous in the east being only minor in area.

The contact between the alkaline volcanics and the sandstones is generally at about 2,000 feet above sea level. The constancy of this level suggests that the Triassic was peneplaned before the extrusion of the alkaline lavas.

STRUCTURE

The boundary between the Permian and Carboniferous:

Hanlon (1948b) states that in the area to the south of Kaputar "the boundary between the Carboniferous beds and the Permian beds is in the nature of a thrust fault. The zone of thrust faulting has now been traced continuously from the Werrie basin (Carey, 1934) through the southern part of the Country of Nandewar (Lloyd, 1933; Hanlon, 1948a), to the Nandewar Mountains."

The present writer has traced the Permo-Carboniferous boundary to the north of the area investigated by Hanlon (1948b), who traces the fault, trending north-west in the north of the County of Nandewar, to Black Mountain, east of Mt. Deriah, where it is obscured by the lavas.

Hanlon (op. cit., p. 307) further states "From a point between Black Mountain Creek and its tributary Basin Creek, in the Parish of Rusden, County of Nandewar, where the fault is obscured by Tertiary igneous rocks, it must swing away to the north. If it continued in a north-westerly trend it would cross Eulah and Bullawa Creeks and could not fail to be identified."

The fault has not been found in Eulah Creek, but Carboniferous rocks have been found in the Upper reaches of Bullawa Creek, while Jensen (1907) reported the presence of Carboniferous rocks in Boomi Creek, a Creek over the range to the east from Bullawa Creek. This would suggest that the Western Thrust as mapped by Hanlon (1948b) changes its direction from north-west to nor-north-west and passes under the lavas just west of Coryah Gap, continuing nor-north-west

across Bullawa and Oakey Creeks, under the lavas in the mountains to the north, passing east of Mt. Lindesay, and emerging to the south of Nobby's.

West of Nobby's the appearance of many dykes and sills show that the region has suffered intense intrusion by alkaline rocks, the place of intrusion being localized by the pre-existing fault. Many minor faults, striking N30°W, exist in the vicinity. Carboniferous beds exist to the east of the disturbed belt, and in the west, at the bottom of Killarney Gap, Permian beds outcrop. The fault must pass through this belt to the west of Nobby's. It then perhaps strikes north-west towards Mt. Bobby Waa, and through the mountains to the north. Any possible outcrop of the Fault north of the Nandewar Mountains is obscured by Mesozoic beds.

The change of strike of the fault would seem to indicate that there is not one fault, but a series of faults arranged en echelon, giving a broad zone of faults.

Hanlon (1948b) states that the age of the thrusting is post Lower Coal Measures. Since unfaulted Mesozoic beds cap the Permian to the west of the fault and the Carboniferous to the east, the faulting can be no younger than Mesozoic.

Much movement has taken place along the fault with the Tertiary volcanism. The fault formed the structural weakness which localized later volcanic action, and the area near the fault is now covered with trachyte intrusions.

ANALCITITE WITH ULTRABASIC XENOLITHS

The rock consists of an analcitite matrix with from 60-75 per cent of peridotite xenoliths, and xenocrysts of olivine and pyroxenes. It occurs as a 1 to 3 feet thick sill intruding Permian beds dipping S.E. 25° in Dingo Creek, a tributary of Bullawa Creek. The outcrop is about 250 yards upstream from the junction of Dingo and Bullawa Creeks. Only about 40 feet of the sill is exposed in the bank of Dingo Creek. The occurrence has been described by Jensen, (1907, p. 855); and Wilshire and Binns (1961).

Jensen named the rock a lamprophyric (monchiquite) porphyry, recognising the xenolithic nature of the fragments. He also carried out a bulk analysis of the rock and xenoliths but this analysis is obviously of little value (Table 2 , No. 9).

Wilshire and Binns (1961) studied this occurrence, together with others of this type in N.S.W. They state that this sill forms a feeder to part of the later alkaline extrusives of the Nandewars, but this is not so, since the analcitite is markedly undersaturated with respect to SiO_2, while the later extrusives are all saturated or oversaturated. The analcitite matrix shows closer affinities mineralogically and chemically to the teschenites in the vicinity, and is considered to have been intruded at approximately at the same time. Thus the analcitite is not connected with the later mountain building alkaline extrusives.

Both Wilshire and Binns (1961) and Jensen (1907) call this rock a lamprophyre. The term lamprophyre implies a strongly porphyritic intrusive rock, with ferromagnesian phenocrysts set in a base of either felspar

or felspathoids (Hatch, Wells and Wells, 1951, 348-349; Turner and Verhoogen, 1960, 251). This rock, excluding the xenocrysts, is fine grained and has abundant analcite and nepheline in the groundmass, with little or no felspar, and is more correctly termed analcitite.

Petrography

Analcitite Base:

Fine grained, the groundmass makes up about 40 per cent of the rock. Abundant euhedral small crystals of titanaugite are set in a mass of analcite, minor nepheline, and very minor alkali felspar. Small crystals of reddish biotite are quite abundant, and melilite is possibly present.

Coarser grained ocelli, with an analcite - nepheline base, are common. Biotite crystals, and elongate, often hoop-shaped crystals of titanaugite, some with aegerine-augite rims, and sparse discrete crystals of aegerine-augite are all set in the felspathoid base. The titanaugite crystals are zoned, with normal and hour-glass colour zoning, and have quite an intense purple colour, indicating a high content of TiO_2.

Xenoliths and xenocrysts:

The extreme abundant (60-75 per cent) and the great variety of the xenolithic fragments are the most typical features of this rock. The xenoliths and xenocrysts reach up to 2 inches in length, and some of them are quite angular.

Varieties of xenoliths recognised are:

1. Gabbro or granulitic xenoliths: These have granular allotriomorphic texture, reminiscent of layered basic and ultra-basic intrusions. Plagioclase (An_{66}) is very abundant, and is complexly twinned on the albite,

pericline, and carlsbad laws. The twin lamellae are often bent, and the plagioclase shows signs of strain. This again, is similar to the lower layers of stratified basic and ultrabasic intrusions, where the weight of superincumbent layers produces strain effects. Granular hypersthene crystals are present with moderate pleochroism of the type:

X = pale red, Y = pale pink, Z = pale bluish green.

$2V_{\alpha} = 50\text{-}60^{\circ}$.

Low birefringence.

From the graph of Deer, Howie and Zussman (1963, vol. 2, Fig. 10) a composition of roughly Fs_{30-40} is indicated.

Chrome diopside crystals, bright green in hand specimen, are pale green under the microscope, not appreciably pleochroic, with $2V_{\gamma} = 40\text{-}50^{\circ}$, and a maximum extinction angle of $Z \wedge c = 40^{\circ}$.

Brown spinel crystals, possibly enriched in Cr_2O_3, are present, and are altered to a pale brown mineral, and opaque oxides.

The approximate mode of the granulite is:

50 per cent plagioclase, 22 per cent hypersthene, 22 per cent diopside, 5 per cent spinel, 1 per cent rest.

2. Peridotite xenoliths: These are the most common xenoliths present, and there is a greater variety within the broad classification of the peridotite type. These xenoliths typically have granular allotriomorphic texture with large crystals of olivine, which usually have been moderately to extensively altered to carbonates by the analcitite magma. The pyroxene crystals, where present, tend to be slightly poiklitic towards the olivines. No felspars are present, and spinels are rare.

Wilshire and Binns (1961) give modes of two peridotite xenoliths in the analcitite:

1. Olivine 85.4 per cent, clinopyroxene 14.6 per cent,

2. Olivine 58.3 per cent, clinopyroxene 41.0 per cent, mica 0.5 per cent, magnetite 0.2 per cent.

The following types of peridotite have been recognised:

Harzburgites: made up of olivine (altered and shattered) with 2V approximately 90°, orthopyroxene with $2V_{\alpha} = 60-70^{\circ}$, and with small reaction rims.

Peridotites - wehrlites: consisting of olivine, colourless to pale green diopside - salite with $2V_{\gamma} = 40-50^{\circ}$ and maximum extinction angle 40°. The diopside is slightly poiklitic towards the olivine, and exsolution lamellae, presumably of orthopyroxene, have developed in the diopside.

Peridotite xenoliths with both olivine, orthopyroxene, and clinopyroxene, are found.

Mica peridotites: consisting largely of quite fresh olivine and phlogopitic mica, with pleochroism:

X = straw yellow, Y = Z = deep red.

Wilshire and Binns (1961) have carried out optical determinations on the olivine and clinopyroxene from the Nandewar peridotite xenoliths and find:

	α	β	γ	$2V_{\gamma}$	Composition
Olivine	1.656	1.674	1.691		$Fo_{89}Fa_{11}$
Clinopyroxene	1.682	1.688	1.711	$52^{\circ}-55^{\circ}$	$Ca_{44}Mg_{45}Fe_{12}$

Measurement of olivine refractive indices by the present author gave a range of from $\beta = 1.673$, Fa_{10}, to $\beta = 1.678$, Fa_{12-13}.

One accidental sedimentary fragment has been found in the analcitite and this is a quartzite which has been recrystallised, but still retains vestiges of former bedding.

Xenocrysts:

1. Olivine xenocrysts, which are quite often altered to, and pseudomorphed by carbonate, are quite common. These crystals are often euhedral and can be up to 1/2" in size. The range of composition as indicated by refractive indices is the same as for the olivines from the peridotite xenoliths - Fa_{9-13}.

2. Diopside and titanaugite xenocrysts are common. Pale green diopside xenocrysts, up to 1 1/2" long and relatively euhedral with reactions rims of titanaugite, are accompanied by titanaugite xenocrysts, which are of similar size, pale mauve with deeper mauve reaction rims.

Wilshire and Binns (1961) have analysed a clinopyroxene xenocryst from the analcitite (op. cit., Tables 4a and 4b, No. 3) and the present author has also analysed a titanaugite xenocryst from the same rock (Plpx). The comparative optics and chemistry have been discussed in the section devoted to the pyroxenes. It is sufficient to say here that the chemistry of the clinopyroxene analysed by Wilshire and Binns indicates a composition of $Ca_{45.5}Mg_{36.8}Fe_{17.7}$ while the clinopyroxene Plpx analysed by the present author has a composition of $Ca_{42.8}Mg_{44.1}Fe_{13.1}$. This emphasises the variable chemistry of the pyroxene xenocrysts, a point also indicated by the optics; the β refractive index from Wilshire and Binns being 1.712, whereas the clinopyroxene Plpx has $\beta = 1.693$.

In some of the smaller clinopyroxene xenocrysts, the crystals merely consist of a core turbid with inclusions, with a deep reaction rim of

purple titanaugite.

Some rare orthopyroxene xenocrysts occur with similar reaction rims to the diopside xenocrysts. Sometimes the orthopyroxene xenocrysts react with the magma to give many small olivine crystals, with a titanaugite rim to the whole cluster of crystals. This reaction of the orthopyroxene with the undersaturated analcitite magma is to be expected according to Bowen - Anderson reaction (Bowen and Anderson, 1914).

3. Biotite: Some large rounded xenocrysts of biotite occur as "books" of polymorph 2M (Wilshire and Binns, 1961). An analysis was made of this biotite to determine whether it is a xenocryst, or a phenocryst, and this analysis for both major and trace elements Ba, Sr, and Rb is set out in Table 5 , together with the structural formula and optical properties of the mineral.

The high Mg of the biotite, together with the rather low iron, indicates a composition close to phlogopite in the biotite - phlogopite series, with a formula:

$$(K, Na, Ba)_{2.119}\ (Fe^{2+}, Mn)_{0.964}\ (Mg)_{3.612}\ (Fe^{3+}, Ti, Al)_{1.330}$$

$$Si_{5.403}\ Al_{2.597}\ OH_{1.251}\ O_{22.749}$$

There is thus mainly a substitution of Mg for Fe^{2+} in the octahedral sites in the lattice.

Heinrich (1946) has drawn a graph of γ refractive index against composition for the biotite - phlogopite series. Since the γ and β refractive indices are almost equal in value, a plot of the β index gives, approximately, the values of FeO, Fe_2O_3, and TiO_2. Heinrich (op. cit.)

TABLE 5

ANALYSIS OF PHLOGOPITIC BIOTITE XENOCRYST FROM ANALCITITE, DINGO CREEK, NANDEWARS. ANALYST M.J. ABBOTT.

(Major elements wt. per cent, trace elements ppm by wt.)

SiO_2	36.15
TiO_2	5.81
Al_2O_3	15.83
Fe_2O_3	4.31
FeO	7.64
MnO	0.07
MgO	17.01
CaO	0.59
Na_2O	0.97
K_2O	9.03
P_2O_5	0.10
H_2O^+	2.51
BaO	0.38
Total	100.40
Rb	210
Sr	211
Ba	3372
K/Rb	357

Structural formula based on (O, OH) = 24.000 $X_2Y_6Z_8$ $(O, OH)_{24}$

Si	5.403	8.000
Al	2.597	
Al	0.192	5.906
Ti	0.653	
Fe^{3+}	0.485	
Fe^{2+}	0.955	
Mn	0.009	
Mg	3.612	
Ca	0.094	2.119
Na	0.281	
K	1.722	
Ba	0.022	
OH	1.251	

$\beta = 1.638$

Polymorph 2M (Wilshire and Binns, 1961).

showed that an approximate straight line relationship between γ refractive index and the value $FeO + 2(Fe_2O_3 + TiO_2)$ existed, showing that the effect of Fe^{3+} and Ti^{4+} on the refractive index is twice that of Fe^{2+}. The value of β for the biotite xenocrysts (1.638), together with the $FeO + 2(Fe_2O_3 + TiO_2)$ value (27.9) gives a point which lies very close to the curve of Heinrich (op. cit.).

The high TiO_2 content of the biotite manifests itself as a distinctly red-brown colour (Hall, 1941). In a titaniferous phlogopite from a phlogopite leucite lamproite, West Australia (Prider, 1939), with high TiO_2 (8.97 per cent) most of the Ti is in the octahedral position, and the (OH, F) is unusually low (2.53 per cent). Both these features are duplicated in the biotite - phlogopite from the Nandewar analcitite, where the TiO_2 is also high (5.81 per cent) and all of it is in octahedral positions in the lattice; and the (OH, F) content is low at 2.51 per cent. Prider (1939) has suggested that the low (OH, F) of the phlogopite from the Kimberley leucite lamproite is due to its crystallisation from a dry magma, or to loss of volatiles during intrusion.

Since the analcitite containing the xenoliths in the Nandewars must have been a quite hydrous magma when intruded, the biotite - phlogopite xenocrysts are assumed to have crystallised in a dry environment, presumably in the lower crust, where high metamorphic grade would be attained. Miyashiro (1958) has found that the Ti content of biotite increases with metamorphic grade in regionally metamorphosed rocks. The high Ti of the Nandewar biotite - phlogopite xenocryst is also in agreement with its postulated origin and crystallisation towards the base of the crust.

The ratio of the Mg/Fe^{2+} indicates that the Nandewar phlogopitic

biotite crystallised in a basic to ultrabasic environment (Heinrich, 1946).

The rather low Rb^{+} (210 ppm) of the phlogopitic biotite (which compares with the Sr^{2+} of 211 ppm) rules out the possibility of the mica being a late stage crystallisation product of the analcitite magma.

The Ba^{2+} is high (3372 ppm), since micas provide a favourable site for the acceptance of Ba.

The K/Rb ratio is 357, higher than would be expected from a late stage mineral.

All the evidence indicates that the phlogopitic biotite is a xenocryst which presumably initially crystallised at a level near the base of the crust. The phlogopites in the mica peridotites are expected to have broadly similar chemistry and paragenesis.

Reaction between xenoliths and analcitite:

This reaction between xenoliths and xenocrysts and the analcitite is quite marked and extensive.

The olivine does not appear to react directly with the analcitite magma, and often is only slightly mechanically shattered. Subsequent alteration (possibly deuteric) changes the olivine to carbonates and zeolites, and often only a carbonate pseudomorph remains.

The plagioclase is analcitised, and sometimes is attacked, when a small rim of titanaugite crystals form just inside the margins of the plagioclase crystals.

Spinel is attacked and altered by the analcitite to a dark, opaque material.

The clinopyroxene xenocrysts, which usually have rather pale colour

and extreme dispersion, develop a reaction zone on the margins of the crystals. From the core outwards the titanaugite or diopside passes outwards into a 'spongy' zone, followed by a zone of deeper mauve titanaugite which becomes deeper in colour in passing outwards to the rims of the crystals. This reaction indicates that the clinopyroxenes xenocrysts are not in equilibrium with the analcitite magma.

Petrogenesis and origin of xenoliths:

Wilshire and Binns (1961) in a general study of ultrabasic xenoliths from volcanic rocks in N.S.W. suggest that the occurrence together of peridotite, hornblende - biotite peridotite, pyroxenite, and gabbro indicates a common origin. They add that many of the variants may be due to disintegration of inhomogeneous, banded source rocks.

The possibility of accidental origin of these xenolithic fragments has been rejected by Wilshire and Binns on the grounds of the similarity of the composition of the xenoliths over large areas. The observations of Kuno (1959) that these ultrabasic xenoliths are absent from the tholeiites also seems to rule out accidental origin.

Cognate origin of the xenoliths has been eliminated because of the fabric of the peridotite xenoliths (Wilshire and Binns, op. cit.), and the presence of orthopyroxene, which is not a phase crystallising from alkali olivine basalts (Wilkinson, 1962).

Wilshire and Binns (op. cit.) and Ross et al. (1954) stress the uniformity of mineralogy and composition from widely separated areas. To these workers this uniformity of composition is held to be due to a worldwide source of ultrabasic material, varying little in composition, although the proportions of the minerals may vary. This peridotite material is

further held to be very abundant in the upper mantle.

The very magnesian composition of the olivines (Fa_{11}), together with the presence of translation lamellae parallel to (100); the Mg rich composition of the orthopyroxenes (Fs_{11}, Wilshire and Binns, 1961, Table 5) sometimes with exsolution lamellae of clinopyroxene; the chemistry of the clinopyroxene, with high Al_2O_3 and MgO and large amounts of Tschermak's component (Wilshire and Binns, 1961, Table 4; this thesis, Table 14); and the Mg and Ti rich composition of the phlogopitic biotite with relatively low H_2O all lead to the conclusion that some of the xenoliths have come from a region where temperatures are high, where the granulite facies conditions has been attained (from a study of clinopyroxene compositions, White 1964), and where pressure is moderately high. These are the conditions to be expected in the lower crust - upper mantle region.

Some of the xenoliths in the analcitite are undoubtedly accidental, and are derived from shallower levels in the crust. The gabbro (granulite) xenolith, with its relatively Fe-rich ferromagnesian phases (e.g. the orthopyroxene has greater than 20-30 per cent of the Fs component), together with the large amount of plagioclase, suggests that it has been derived from a layered basic intrusion. From a study of a similar xenolithic fragment in an analcite basalt, Wilkinson (1962) has concluded that it originated from a differentiated mass at depth.

The presence of a large quartzite fragment also suggests that the analcitite has rafted off fragments at quite a shallow depth in its rise to the surface.

The derivation of the alkalies and voltaile enriched analcitite magma directly from the mantle, without some intermediate stage of differentiation,

poses difficulties.

It is therefore proposed that the analcitite has rafted off fragments of material from levels ranging from the upper mantle - lower crust region up into the crust towards the surface, while rising to the surface.

It is noticeable feature that this analcitite has brought no eclogite inclusions to the surface.

TESCHENITES

The teschenites occur as a series of sills and sill-like masses intruding the Permian and Mesozoic. Where the teschenite intrudes the Mesozoic, it forms sills having a regional dip of 5-10° SW conforming with the dip of the sediments. The relation of the teschenite to the Permian sediments is not clear.

In some places the sills are up to 400 feet in thickness, but in many places the sills are faulted and intruded by later alkaline volcanic rocks of the main volcano building phase, and here thicknesses are difficult to determine.

The sills have chilled margins, often unexposed, because of the presence of large amounts of scree. The teschenites of the chilled margins have a fine grained basaltic appearance, in contrast to the coarser doleritic types in the centres of the sills. In some places gabbroic and pegmatitic textural types are observed, these being the extreme differentiates.

To the south of the Nandewar Mountains area much thicker sills are common, but they also intrude Mesozoic rocks, Wilkinson, 1958; Manser, 1960. Wilkinson (op. cit.) notes that the teschenites are frequent field associates of the alkali olivine basalts of New England, which is the parent magma of the teschenites.

Jensen (1907, pp 881-882) named the teschenites "ophitic olivine dolerites" or "ophitic analcite dolerites" and concluded that the teschenite formed large laccolitic masses, one in Dingo Creek, estimated to be 700 feet thick, and another at Killarney Gap, 400 feet thick; but

both these occurrences appear to be sills.

Nomenclature:

Except for some of the contact rocks, all are teschenites as defined by Walker (1923), and Wilkinson (1955). The modal amounts of the constituent minerals vary, but only in the contact rocks is this sufficient to term the rocks other than teschenite.

The contact teschenites have a fine grained basaltic appearance in hand specimen, and are quite rich in mafic constituents, an approximate mode being: 40 per cent titanaugite, 15 per cent olivine, 25 per cent plagioclase 20 per cent titanomagnetite and dusty analcitic mesostasis.

Teschenites rich in olivine have been named picroteschenites and picrites (Tyrell, 1917, 1952; Walker, 1930; Drever, 1953; Wilkinson, 1955; Drever and Johnston, 1958). The teschenites here are, however, much richer in titanaugite than olivine, so it is appropriate to name these rocks at the contacts augite picroteschenites, in the sense of Tyrell, (1952, p. 377).

The textural features shown by the late stage schlieren of teschenite merit the name teschenite pegmatites (Walker, 1930, 368-370).

Textures:

Walker (1923) and Wilkinson (1958) state that three textural types are found with increasing differentiation in teschenite sills:

1. Porphyritic or Basalt type: Phenocrysts of olivine and titanaugite (sometimes glomeroporphyritic), with fine to medium grain.

2. Ophitic or Doleritic type: Non-porphyritic, ophitic to subophitic relations between titanaugite and plagioclase. Grain medium to coarse.

3. Non-ophitic or Gabbro type: Even grained hypidiomorphic texture. In varieties rich in analcite, the titanaugite is euhedral. Grain is medium to coarse.

Wilkinson (1958, p. 5) states "In a general way, these three divisions represent in order (1 to 3) the teschenite sequence with increasing height above the base of the Black Jack sill."

In the Nandewars the sequence of textural types (1 to 3) is found from the margins of the sills (both top and bottom) towards the centre; while, as mentioned before, pegmatitic types are occasionally encountered.

The chilled contact teschenites, not seen in the Black Jack sill, have a basaltic, fine grained texture, being non-porphyritic. These rocks feature euhedral titanaugite crystals, often in glomeroporphyritic aggregates; and relatively large amounts of dusty iron charged mesostasis.

Mineralogy

Olivine:

Olivine is present in all the teschenites except the teschenite pegmatites, but it is usually completely altered and pseudomorphed by serpentine minerals in the gabbroic teschenites.

The composition of the olivines varies from Fa_{15} ($\beta = 1.682$) in the upper chilled contacts, although a range of from Fa_{13} ($\beta = 1.676$) to Fa_{17} ($\beta = 1.687$) has been found in the upper contact teschenites on Killarney Gap; through to Fa_{19-23} ($\beta = 1.690 - \beta = 1.700$) in the olivine

phenocrysts in the more differentiated porphyritic teschenites away from the margins; to Fa_{30} ($\beta = 1.715$) in the ophitic teschenites. Zoning of the olivines is present in the porphyritic and ophitic teschenites, but no attempt was made to measure the extent of enrichment in fayalite in the margins, partly because the margins nearly always suffer incipient alteration.

Zoning from a forsteritic core to a fayalitic margin is typical of teschenites (Wilkinson, 1956).

The most magnesian composition (Fa_{13}) was found in the upper chilled margin, although some 20-30 feet below this, the olivines had changed with differentiation to Fa_{30}. This indicates that the teschenite rapidly chills at the margins when intruded but then solidifies from the bottom of the sills upward, the volatiles and alkalis being forced upward. This keeps all but the chilled margin at the top liquid until the latest stages of crystallisation. Furthermore, both the gabbroic and pegmatitic types have been found near the top of the sills.

Clinopyroxene:

This is always a pale mauve member of the diopside salite series. The pleochroism, which is never very marked, is: X = mauve (Yellowish), Y = pale reddish violet, Z = mauve (reddish). The refractive index of the contact teschenite clinopyroxene is $\beta = 1.698$.

The titanaugite shows great variation in habit. Both normal and hour-glass zoning is present in the coarser grained rocks.

In the basaltic contact rocks the titanaugites are dominantly small and euhedral, sometimes forming glomeroporphyritic aggregations; while

in the ophitic teschenites, the titanaugites are larger, and have ophitic relations with the plagioclase. Where the titanaugites adjoin areas of analcitic mesostasis, green aegerine-augite rims are developed. Some twinning parallel to (100) is seen.

In both the gabbro and pegmatitic teschenites the titanaugites are larger in grainsize and have ophitic textural relations, green aegerine-augite rims being common; while more chloritisation of the clinopyroxene occurs due to late stage deuteric activity.

Plagioclase:

In all specimens this forms elongated laths (elongated parallel to C) of varying sizes, with Albite, Carlsbad, and rare Pericline twinning. Except in the chilled margins, the plagioclase has ophitic relations with the titanaugite, which is indented by the plagioclase laths. The plagioclase is zoned, with more albitic rims, the extent of the zoning being greatest in the pegmatitic teschenites.

The compositions of the plagioclases have been determined by the maximum symmetrical extinction angle perpendicular to (010) using the graphs of Winchell and Winchell (1951, p. 262, 283). The accuracy of these measurements is not expected to be greater than $\pm$ 4 per cent molecular Ab or An.

The most calcic plagioclases, An_{68}, occur at the chilled margins of the sills. The plagioclase, in general, becomes more sodic with increasing differentiation, and the extent of zoning and grainsize also increase at the same time. Typical compositions of the plagioclases are:

Porphyritic and Basaltic teschenites:			An_{68}
Ophitic	"	":	An_{60-52}
Gabbroic	"	":	An_{54}
Pegmatitic	"	":	An_{60-45} (zoned xtal)

The analcitisation of the plagioclase becomes more advanced in the gabbroic and pegmatitic teschenites. All the plagioclase laths include myriad elongate crystals of apatite.

Iron-Titanium oxides:

These opaque oxides are present in all the teschenites, and they can be referred to homogeneous Ti-rich magnetite -- an Fe_2TiO_4-Fe_3O_4-$FeTiO_3$-Fe_2O_3 solid solution (Nicholls, 1955; Wilkinson, 1957b.). Wilkinson reports that this solid solution is homogeneous in the Black Jack sill, and terms it titanomagnetite.

In the contact teschenites, the titanomagnetites either form extremely small cuboids or skeletal and dendritic crystals in the mesostasis.

The iron titanium oxides of the contact teschenite from the upper contact have been examined in polished section, and have also been X-rayed (Co $K_{\alpha 1}$ radiation) to determine the nature of certain inclusions and also to enable the unit cell dimensions to be calculated.

The small, euhedral crystals, which are slightly anisotropic, are accompanied by dendritic and skeletal crystals in the mesostasis. These latter crystals in reflected light are pleochroic and strongly anisotropic, and have some patches of blue alteration or exsolution products, and from X-ray examination it is suspected to be brookite or pseudobrookite.

The smaller euhedral crystals are similar to those in the Black Jack sill (Wilkinson, 1957b) in being isotropic (or only faintly anisotropic)

and homogeneous without exsolution lamellae of ilmenite. The skeletal titanomagnetites, revealing enrichment in $FeTiO_3$ by their anisotropism and pleochroism, appear to be quite distinct.

The unit cell edge of the titanomagnetite is 8.45 Å. The diffraction lines are sharp and show no diffuseness or doubling. The cell edge is larger than that for pure magnetite (Deer, Howie, and Zussman, 1962, vol. 5, pp. 72-73, Table 12).

In the porphyritic teschenites, larger ophitic titanomagnetites, intergrown with the plagioclase and titanaugite, are found, as well as the two former types. The ophitic titanomagnetites often have a rim of titanbiotite. In the ophitic teschenites, most of the titanomagnetites are larger and have ophitic texture. In the gabbroic teschnites, large skeletal forms are found as well as the other types mentioned above. In all these titanomagnetites no extensive leucoxenation has occurred.

In the teschenite pegmatite, the large crystals of titanomagnetite are preferentially altered to laucoxene along (111) planes, indicating unmixing of the homogeneous titanomagnetite into an Fe_3O_4-Fe_2TiO_4 rich component, and an $FeTiO_3$-Fe_2O_3 rich component, the ilmenite rich component being subsequently altered to leucoxene.

The extent of idiomorphism of the magnetite decreases with later crystallisation.

Analcite:

This mineral may be either primary or secondary. When primary, it occurs interstitial to the unaltered plagioclase laths, is clear, isotropic and includes crystals of apatite. In the chilled contact rocks there is a

large amount of highly analcitic interstitial mesostasis, consisting of dendritic titanomagnetites, crystallites of titanaugite and aegerine-augite, apatites and chlorite set in the analcite base.

The great bulk of the analcite in the teschenites is primary; but in some of the rocks, secondary analcite also occurs, forming either small pale yellow vughs with many inclusions, or analcitised margins of former plagioclase crystals.

In the teschenite pegmatite the analcite is not isotropic, but has a low D.R., is completely twinned, and has a $2V^{-}$ of 60° in places. Coombs (1955) states that non-cubic birefringent analcite has twinning parallel to the pseudo-cubic (110) planes - six sets of dodecahedral twin lamellae exist. Analcite similar to this has been seen in the pegmatitic teschenite.

Parts of the analcite are isotropic, others are anisotropic, and some are biaxial. This suggests that the analcite has inverted from a higher symmetry "strictly cubic form existing in the presence of water vapour at moderately elevated temperatures to one or more forms of lower symmetry stable at ordinary temperatures ..... The fact that analcime is shown to exist at ordinary temperatures with varying departures from cubic symmetry suggests that in its case transformations tend to be more sluggish or complicated so that we see the products in various arrested states". (Coombs, 1955, p. 704).

The cross hatched twinning in the analcites recalls the secondary twinning "readily produced by inversion processes in anorthoclase, leucite and other minerals." (Coombs, op. cit., p. 706)

Steiner (1955) suggests that on inversion, analcite loses K_2O, while Wilkinson (1958) notes that K_2O decreases with increasing

differentiation.

Apatite:

This mineral forms extremely elongated prisms and needles which increase in size with differentiation, the largest apatites being in the gabbro and pegmatitic teschenites. This points to an increase in volatile content with differentiation.

The apatite needles are confined to the plagioclase laths, analcite and mesostasis, suggesting late stage crystallisation.

Biotite:

Found mostly in the contact teschenites, it forms rims to titanomagnetites, and also occurs as small discrete crystals. The pleochroic scheme is:

Y = maroon, X = pale yellow brown, Z = dark red brown; $X < Y = Z$.

X = pale yellow, Y = dark brown, Z = reddish brown; $X < Z = Y$.

The reddish colour can be correlated with high TiO_2 (Hall, 1941; Hayama, 1959).

Alkali Felspar:

Was detected only in the pegmatitic teschenites, where it occurs as rims on the plagioclase laths and as discrete stumpy crystals of anorthoclase. The anorthoclase ($2V^- = 60^\circ$) has subsequently unmixed sanidine ($2V^- = 20^\circ$) which tends to migrate to the crystal boundaries. This unmixing has occurred in both the rims of anorthoclase and in the discrete crystals.

Calcite:

In the pegmatitic teschenites primary calcite occurs with well defined

outlines, forming large discrete crystals. It is interstitial in its mode of occurrence. Because the rocks are enriched in iron, it is probably sideritic.

Mesostasis: is present in all the teschenites.

In the contact teschenites, large amounts of duty analcitic mesostasis, charged with crystallites of titanomagnetite, and titanaugite, represent the chilled liquid solidified after extrusion.

In the more differentiated teschenites the mesostasis represents the volatile enriched, late stage residuum, and crystallises to a mixture of analcite and apatite, with some titanomagnetite. Chlorite and calcite are also common. The mesostasis increases in amount with differentiation.

Alteration products:

The olivine alters to bowlingite, a brown green mineral (Wilkinson, 1958), and iddingsite, deep ruby-red material. Iddingsite is not regarded as a valid mineral (Ming Shan Sun, 1957; Wilshire, 1958; Brown and Stephen, 1959; Smith, 1959), but a mixture of goethite and chlorite or hematite and quartz. Furthermore, Nagy and Faust (1956, p. 285) consider that bowlingite is not a valid mineral species, but that it is a mixture of chrysotile and antigorite. The other ferromagnesian minerals suffer chloritisation, the plagioclase alters to calcite, and sericite and kaolin also occur as alteration products.

Several modal analyses have been made of the teschenites, and these have been systematically related to their positions in the sills.

The main trends shown by the modes can be summarised as follows:

1. Concentration of clinopyroxene and olivine near the chilled

contacts. The clinopyroxene constitutes 40 per cent of the contact rocks, and olivine 20 per cent. These two minerals both decrease in amount away from the chilled contacts towards the more differentiated parts of the sills, the clinopyroxene decreasing to 20 per cent in the pegmatitic teschenites, and the olivine disappearing altogether in these rocks.

2. The plagioclase ranges from 25 per cent in the chilled margins, where it has an average composition of An_{65}, to 45 per cent in the pegmatitic teschenite, where the plagioclase of composition An_{45} is accompanied by alkali felspar. The analcitic mesostasis ranges from 6 per cent in the contact rocks, to 20 per cent in the pegmatitic teschenites. In the contact rocks, the dusty mesostasis is iron charged because of the large amount of very fine granules of iron oxide minerals, whereas in the differentiates it is much richer in analcite.

Apatite is also quite abundant, but has been included with the plagioclase in the modes, since the apatite needles usually lace the felspars.

The decrease in olivine and titanaugite, together with the increase in plagioclase, alkali felspar, and analcitic mesostasis, shows that on differentiation of the teschenites, the MgO and FeO decrease (although the FeO/MgO ratio increases with differentiation as the olivines become more fayalitic), while the Na_2O and K_2O increase.

The trends parallel those found by Wilkinson (1958) for the Black Jack sill, apart from the contact teschenite, which is finer grained and has almost twice as much clinopyroxene as the Black Jack teschenite B1 (Wilkinson, 1958, Table 2). The clinopyroxene in the Black Jack sill

increases in amount upwards from the lower contact (Wilkinson, 1958, Fig. 3), but in the Nandewars the clinopyroxene decreases in amount away from both the top and bottom chilled contacts towards the centre of the sills.

The rocks taken by Wilkinson (1958) to be the contact rocks of the Black Jack sill, are, as stated by him (op. cit., p. 5) not chilled selvages, but are the nearest approach to the contact, which is obscured by scree slopes. Also, the top of the sill has been eroded away.

The present author has been fortunate in being able to locate in several places in the Nandewar Mountains area very fine grained teschenites, representing the chilled margins of the sills. Both upper and lower contacts have been found in various localities.

A chilled contact teschenite from the upper contact of the sill was selected for analysis to avoid the possibility of analysing an accumulative rock. This sill intrudes a Triassic sequence (Hanlon, 1948b) which lies unconformably on folded Carboniferous beds, the Rocky Creek Conglomerates (McKelvey and White, 1964).

The teschenite was collected just to the east of Mt. Bobby Waa at 30°05'S 150°08'E. The fine basaltic texture and grainsize leads to the conclusion that this contact rock was entirely liquid at the time of emplacement. Wilkinson (1958, p. 28) is of the opinion that the contact rocks he collected from the Black Jack sill were not entirely liquid when intruded.

The analysis and norm of the contact teschenite is set out beside the data from Wilkinson (1958) for teschenites B1 and B2 from the Black Jack sill in Table 6 . The trace element contents, determined by X-ray fluorescence are set out beside the trace element data for the Black Jack

TABLE 6

CHEMICAL ANALYSES OF A CHILLED CONTACT TESCHENITE (CTS) FROM THE NANDEWAR MOUNTAINS, COMPARED WITH ANALYSES OF CONTACT TESCHENITES B1 AND B2 FROM WILKINSON (1958, TABLE 6), FROM THE BLACK JACK SILL.

	CTS	B1	B2
SiO_2	45.20	44.78	44.73
TiO_2	2.42	2.49	2.58
Al_2O_3	13.39	14.03	14.42
Fe_2O_3	2.97	4.15	2.93
FeO	8.81	9.15	9.51
MnO	0.19	0.14	0.15
MgO	10.20	9.57	8.08
CaO	10.12	8.12	8.31
Na_2O	2.51	3.30	3.60
K_2O	1.80	1.77	1.96
P_2O_5	0.73	0.62	0.64
H_2O^+	1.60	2.05	2.89
H_2O^-		0.14	0.23
CO_2	0.01	nt.fd.	nt.fd.
SrO	0.10		
ZrO_2	0.03		
BaO	0.05		
Total	100.13	100.31	100.03

CIPW NORMS

		CTS	B1	B2
or		10.64	10.56	11.68
ab		14.60	18.34	16.77
an		19.95	18.07	17.24
ne		3.59	5.11	7.38
wo	di	10.61	7.77	8.47
en	di	7.05	5.20	4.90
fs	di	2.80	1.98	3.17
fo	ol	12.86	13.16	10.50
fa	ol	5.63	5.71	6.32
il		4.60	4.71	5.02
mt		4.31	6.03	4.18
ap		1.73	1.34	1.34
cc		0.02		
H_2O		1.60	2.19	3.12
Rest		0.18		
Total		100.17	100.17	100.09

CTS Chilled contact teschenite from an upper contact, Gulf Creek, Nandewar Mountains, Analyst M.J. Abbott.

B1 Teschenite from the Black Jack sill, Gunnedah, 20 feet above lower contact. Wilkinson (1958, Table 6).

B2 Teschenite from the Black Jack sill, Gunnedah, 20 feet above lower contact. Wilkinson (1958, Table 6).

rocks B1 and B2 (Wilkinson, 1959), which were determined by optical spectrography (Table No. 7). Although optical spectograph determinations do not have the same precision as the X-ray values, the data is of comparative value.

The chemical analysis of the Nandewar contact reveals, as expected from the high content of clinopyroxene in the mode, higher MgO and CaO values than the Black Jack rocks B1 and B2, and appreciably lower Na_2O as expected from the lower modal plagioclase. The total Fe is also lower, and this is reflected into the more forsteritic nature of the olivine, which is Fa_{15} in the Nandewar contact teschenite, and Fa_{21} in the Black Jack contact rocks (Wilkinson, 1958).

When the oxides $FeO + Fe_2O_3$, $Na_2O + K_2O$, and MgO are plotted on an AFM diagram, the Nandewar contact teschenite plots further towards the Mg-rich corner than B1 or B2 (Wilkinson, 1958, p. 25, Fig. 5).

Trace Elements:

The Zr contents of the Nandewar contact teschenite and those from the Black Jack sill (B1 and B2) are comparable (Table No. 7). Wilkinson (1959) has found that most of the Zr occurs in the pyroxene, replacing the Ca(Wager and Mitchell, 1951).

The Black Jack teschenites (B1 and B2) have almost twice the amount of Sr than the Nandewar contact teschnite, whereas the Ba of the Nandewar teschenite is higher by about 100 ppm than in the Black Jack rock, B2. Ba^{++} ($r = 1.34$ Å) tends to follow Ca, and from data in other provinces (Heier and Taylor, 1959) Ba behaves similarly to Sr, decreasing at a more rapid rate than Sr with differentiation. Wilkinson (1959) states

TABLE 7

TRACE ELEMENT DATA FOR A CHILLED CONTACT TESCHENITE (CTS) FROM THE NANDEWAR MOUNTAINS, COMPARED WITH TESCHENITES B1 and B2 FROM WILKINSON, (1959, TABLE 8).

(All expressed in parts per million by weight)

Element	r (in Å)	CTS	B1	B2
Zr^{4+}	0.79	206	250	200
Sr^{2+}	1.12	847	1500	1500
Ba^{2+}	1.34	421	275	325
Rb^{+}	1.47	27	30	70
K/Rb		532	500	233
Ba/Sr		0.5	0.2	0.2
Ca/Sr		855	393	407

CTS Chilled contact teschenite from an upper contact, Gulf Creek, Nandewar Mountains. Analyst M.J. Abbott.

B1 Teschenite from the Black Jack sill, 20 feet above lower contact. (Wilkinson, 1959, Table 8).

B2 Teschenite from the Black Jack sill, 20 feet above lower contact. (Wilkinson, 1959, Table 8).

that Sr replaces Ca in plagioclase and apatite, and the smaller amount of Sr in the Nandewar teschenite can be explained by the much smaller amount of the plagioclase.

The Rb contents of both the Nandewar and Black Jack teschenites are similar, and low. The K/Rb ratio of the Nandewar teschenite is 532, that for the Black Jack teschenite B1 500, while the value of 200 for B2 suggests that the Rb (70 ppm) is too high (Wilkinson, 1959, Table 8).

PETROGRAPHY OF THE ALKALINE ROCKS

BASALTIC ROCKS

Field occurrence

The basaltic shield of the volcano consists of a large number of flows, each 20 to 50 feet thick. Red boles between flows and vesicular tops are common, but there appears to be no great erosional break in the sequence; the basic volcanism is held to have been a succession of quietly extruded flows. To support this, there has been no evidence of any tuffs; Joplin (pers. comm.) believes that tuffs identified by Jensen (1907) in the Nandewars are in fact vesicular basalts.

A remnant of one small spatter cone has been found associated with the flows, where basaltic glass occurs as veinlets and lenticular streaks within the weathered portion of the material of the cone. This spatter cone is only very small, being less than 50 yards wide, and its presence indicates no great violence in the volcanic activity.

The basaltic flows have been extruded onto a peneplaned Mesozoic sandstone surface, and the basalt - sandstone contact has an elevation of 2,000 feet a.s.l. in the portions of the volcanic shield now exposed. On the Kaputar caldera wall, there is a 3,000 feet thickness of basaltic flows.

Cross cutting dykes, plugs, or feeders of basalt have not been found. Presumably these originally existed at the centre of the volcano, but since have been eroded away and also obscured by the later intrusion of trachytes as plugs and domes.

The bulk of the flows of the shield appear to be trachyandesites, with olivine basalts and basalts subordinate. This in direct contradiction

to the recent assertation of Chayes (1963), that intermediate members of the alkali olivine basalt - hawaiite - mugearite - trachyandesite - trachyte - comendite series are scarce in relation to the bulk of the other types. True olivine basalts are extremely rare in this province, considering the great bulk of other basaltic rocks. In the section along the Kaputar Road, only one 50 feet thick flow of olivine basalt has been detected in the 3,000 feet thickness of the basaltic shield.

Petrographically the basaltic rocks may be divided into three broad groups:

1. Porphyritic olivine basalts.
2. Porphyritic 'big felspar' basalts.
3. Non-porphyritic basaltic rocks.

The last group is the most abundant, the 'big felspar' basalts being next in abundance, while, as noted before, the porphyritic olivine basalts are rare.

The trachyandesites appear to be quite persistent laterally, but the 'big felspar' basalts were extruded as a somewhat more viscous lava, undoubtedly due to the large percentage of phenocrysts.

Nomenclature

The nomenclature of the fine grained basaltic rocks is difficult because of several factors. Owing to the extremely fine grainsize, it is impractical to obtain an accurate mode. Since the nature of the felspar largely determines the name to be given to a rock, zoning in the felspars, and the presence of solid solutions of Ab, An, and Or (in potash oligoclases and calcium rich anorthoclases) renders the exact determination of the felspars impossible. These difficulties have been noted before (MacDonald, 1960; Le Maitre, 1962).

The essential mineralogy of the fine grained basaltic rocks is plagioclase of approximately andesine composition (although it is zoned to potash oligoclase), diopsidic pyroxene and opaque iron oxides. According to classical definitions (Johannsen, 1937, p. 160 et. seq.; Hatch, Wells and Wells, 1961, p. 289) these rocks are andesites. However, the usual porphyritic hypersthene-diopside andesites, hornblende andesites and biotite andesites are common in continental orogenic regions and are calc-alkaline; while the non-porphyritic "andesites" of the Nandewars are typically alkaline and quite distinct from the orogenic types.

Several alternative names have been used for andesitic rocks which are alkaline.

The term trachybasalt (Johannsen, 1937, p. 128) implies the presence of calcic plagioclase An $>$ 50, together with orthoclase or anorthoclase. Le Maitre (1962) defines trachybasalt chemically, but notes that Williams et. al. (1954, p. 57) state "orthoclase" or alkali felspar exceeds 10 per cent by volume. The normative felspars of the Gough Is. trachybasalts

($Or_{25}Ab_{48}An_{27}$) can be presented by equal amounts of plagioclase more calcic than An_{50} and alkali felspar (Le Maitre, 1962). The trachybasalts are the most abundant rock type on Gough Island, and are usually porphyritic, with phenocrysts of olivine, clinopyroxene, plagioclase (andesine), alkali felspar and opaques. The total alkalies range from 5 per cent to 8 1/2 per cent.

The trachyandesites on Gough Island (Le Maitre, 1962) have equal quantities of plagioclase (An <50), and alkali felspar, and 'bridge the gap between trachybasalt and trachyte.' Le Maitre uses trachyandesite ' in preference to oligoclase andesite and hawaiite (Macdonald, 1960), as it best preserves the gradational nature of the series' (Le Maitre, 1962, p. 1311). The normative felspar of the average trachyandesite on Gough Island is $Or_{33}Ab_{51}An_{16}$, which can be expressed as equal amounts of alkali felspar and plagioclase less calcic than An_{50}. The total alkalies of the trachyandesites ranges from 8 1/2 per cent to 10 1/2 per cent. Walker and Nicolaysen (1954) also use the term trachyandesite for the rocks of Mauritius.

Thus Le Maitre (1962) uses the terms alkali olivine basalt -- trachybasalt -- trachyandesite -- trachyte for the alkaline lineage on Gough Island. Macdonald (1949, 1960), Muir and Tilley (1961), and Yoder and Tilley (1962) use different rock names for the alkali series on Hawaii. The names which have been used for the saturated and oversaturated alkali series are those pertinent to the problem in the Nandewars.

When Macdonald (1949) named the Hawaiin rocks andesine andesites and oligoclase andesites, other workers assumed 'since both basalts and andesites are present in each, there is no real difference between

the volcanic rocks of the continents and ocean basins. This assertion is supported by reference to my papers on Hawaiian petrography' (Macdonald, 1960, p. 172).

Macdonald advocates the abandonment of the use of the term 'andesite' for oceanic rocks. For those rocks in which the dominant felspar is oligoclase, the name mugearite (Harker, 1904) is appropriate. For those rocks in which the dominant felspar is andesine, Macdonald defines 'hawaiite as a rock with moderate to high colour index, and frequently basaltic habit, in which the normative and modal felspar is andesine, and with soda: potash ratio greater than 2:1. It generally, but not always, lacks normative quartz, and commonly contains normative and modal olivine. Hawaiite is intermediate between alkali olivine basalt and mugearite, and grades into both. It may also be intergradational with the augite andesites of continental orogenic regions, but is markedly distinct from the hypersthenic and hornblendic andesites characteristic of those regions.'

Muir and Tilley (1961) recognise hawaiite as a member of the series alkali olivine basalt -- trachyte. Their definitions of hawaiite and mugearite are based on the type of felspar present' .... we may describe hawaiites mineralogically as being characterised by strongly zoned feldspars ranging from calcic andesine to a feldspar of lime anorthoclase type, the two types of feldspar being present in roughly equal proportions or with plagioclase dominant. In mugearites the plagioclase is more sodic, and the alkali feldspar (lime anorthoclase) is present in greater amount than the plagioclase; less commonly, mugearites may contain interstitial soda sanidine.'

The essential difference between the alkali olivine basalt -- trachybasalt -- trachyandesite -- trachyte series and the alkali olivine basalt -- hawaiite -- mugearite -- trachyte series is in the soda : potash ratio. The latter series of rocks, exemplified by the Hawaiian alkaline series, has a soda : potash ratio of 2:1 or greater, whereas the former series, as on Gough Island, has a soda : potash ratio closer to unity. Therefore in the trachybasalt -- trachyandesite sequence, there is a greater amount of the Or molecule in the norm, and the alkali felspars are richer in potash. In the hawaiite -- mugearite sequence, the alkali felspar is more often a lime anorthoclase of quite sodic composition.

The series of rocks in the Nandewars appears to lie between the two extremes outlined above, and soda : potash is usually 1:1, ranging up to about 1.3:1.

Tilley (in press) has proposed that the soda-rich trachyandesites be called glenmorites, after Glen Mor in Mull, where these rocks are common. The potash-rich trachyandesites are termed tristhanites, after the types on Tristhan de Cunha.

The fine grained basaltic rocks in the Nandewars with significant normative or (10 per cent - 15 per cent) and with modal potash oligoclase and perhaps calcic anorthoclase, and lacking olivine, shall be called trachyandesites.

Petrography

Porphyritic Olivine Basalts:

In hand specimen these rocks possess conspicuous phenocrysts of plagioclase set in a fine groundmass.

Microscopically they are porphyritic, with euhedral phenocrysts of olivine, titanaugite and plagioclase set in a fine groundmass of small plagioclase laths, titanaugites and opaque iron oxides.

The euhedral olivine phenocrysts, usually altered along the margins to iddingsite, have a composition of Fa_{23-24} (β = 1.698 - 1.700), measured from the cores of the crystals. The margins would be more iron rich, but the composition could not be determined because of the alteration.

The clinopyroxene phenocrysts are pale mauve, often with colour zoning, and have α = 1.701 - 1.703, β = 1.705 - 1.707, γ = 1.727, $2V_\gamma = 53^\circ$, and dispersion r > v moderate. The optics indicate little measurable enrichment in hedenbergite or acmite, and the composition is diopsidic.

The plagioclase phenocrysts are extensively zoned and range in composition from An_{67}, β = 1.566 in the cores, to An_{55}, β = 1.560, at the margins. The $2V_\gamma$ of the plagioclase core An_{67} is 78°, indicating high temperature optics from the curves of Smith (1956), in Deer, Howie and Zussman, (1963). The plagioclase has albite and carlsbad twinning with occasional pericline twinning.

The plagioclases in the groundmass range in composition from An_{45-25} (from extinction angle measurements). Carlsbad twins are common, and some albite twinning is present in the larger crystals.

The plagioclases of the groundmass are laced with apatite fibres, which are extremely elongated.

The clinopyroxenes in the groundmass are very small euhedral crystals elongated parallel to the 'c' crystallographic direction. They have a very pale brown colour.

Titanomagnetite crystals, with ragged outlines, are also common in the groundmass, and some small crystals of reddish titanbiotite are sparingly present.

"Big Felspar" Basalts:

These rocks are very distinctive in hand specimen, consisting of large white phenocrysts of plagioclase up to 2" long set in a black fine grained groundmass. The amount of the plagioclase phenocrysts varies from about 5 per cent to 50 per cent.

Microscopically the rocks appear porphyritic, with the largest phenocrysts of plagioclase, and some smaller phenocrysts of titanaugite while some entirely altered microphenocrysts of olivine appear in some of the rocks. The phenocrysts are set in a fine groundmass of small plagioclase laths, magnetite and augite crystals, mostly in pilotaxitic structure; but some of the basalts have trachytic flow structure.

The euhedral plagioclase phenocrysts are zoned, usually in an oscillatory manner, becoming generally more sodic towards the rims. The composition of the cores are generally about An_{67} ($\beta = 1.566$) and extinction angle measurements indicate a range of composition to An_{40} at the margins, which may be slightly resorbed, and with inclusions just inside the margins of the phenocryst. Albite and carlsbad twins are

almost exclusively developed, with some rare Pericline twins.

Titanaugite phenocrysts are usually present in small amount, and these may be zoned with hour-glass and normal zoning. The refractive index (β = 1.706) indicates a composition close to diopside.

In the groundmass, laths of plagioclase and small euhedral crystals of clinopyroxene and magnetite occur.

The composition of the plagioclase, based on extinction angle measurements, ranges from An_{40-50}. Carlsbad twins are most common, but some albite twins are present.

The clinopyroxene crystals, euhedral and elongated parallel to the 'c' crystallographic direction, are pale brown to colourless, and have and have little alteration.

Magnetite crystals, often ragged in outline, are abundant in the groundmass. Elongate apatite needles are present in the plagioclase laths, while some rare deep mauve crystals of titanbiotite ? occur.

These rocks usually suffer advanced alteration, with much chlorite present in the groundmass, and secondary carbonate also.

Trachyandesites:

In hand specimen these rocks are fine grained, black, and have a characteristic 'sheen' owing to the trachytic flow structure in the felspars.

Microscopically they are non-porphyritic, although microphenocrysts of plagioclase can occur. The bulk of the rock consists of small laths of plagioclase with trachytic flow structure, euhedral augites elongated in the 'c' crystallographic direction, and cubes of titanomagnetite. Occasional pseudomorphs after olivine occur. The plagioclase is often

laced with apatite needles.

The plagioclase microphenocrysts when present have a composition of An_{59-60} ($\beta = 1.563$) and usually have albite twinning. These microphenocrysts sometimes show signs of reaction with the magma, suggesting disequilibrium upon extrusion. Many of the microphenocrysts are crowded with minute inclusions. Potash oligoclase rims on some of the plagioclase laths are also possibly present, these margins being untwinned. Joplin (1964, p. 60) suggests that these corroded phenocrysts may be xenocrystal.

The composition of the groundmass plagioclase is difficult to determine because of the fine grainsize, but a range of from An_{50} ($\alpha = 1.556$) to An_{35} ($\alpha = 1.547$) is indicated. Extinction angles of the simple Carlsbad twins support this range of composition. The more sodic compositions probably also contain sizeable amount of potash in solid solution, because of the high K_2O of the rocks. The presence of interstitial felspar, untwinned and with low D.R., suggests the presence of alkali felspar, possibly a calcic anorthoclase.

The microphenocrysts of titanaugite are very pale mauve with $\beta = 1.703$. Pale euhedral crystals elongated parallel 'c' crystallographic direction are quite abundant in the groundmass and make up nearly all the clinopyroxene in the rock.

TRACHYTIC ROCKS

The field occurrence of the broad group of rocks here termed trachytic is much more varied than for the basaltic types.

Dykes intrude the basaltic flows on the Kaputar Plateau; they also intrude the Carboniferous near Rocky Creek; and dykes occur in the Mt. Grattai - Castle Top Mountain area. As the dykes become more massive and bulbous, they begin to take the form of plugs, and these are also quite numerous. Some of the plugs possess very well developed vertical columnar jointing, while others (the Governor) have platy horizontal joints. Both the dykes and plugs tend to be prominent in outcrops, especially when intruding basaltic rocks.

Several round to oval shaped outcrops of trachytic lava possess the typical structure of domes as outlined by Williams (1932). Dome is a general term for domed-shaped extrusions, while steep sided domical intrusions are called "tholoids" (Williams, op. cit., p. 53; Cotton, 1944, p. 158).

Williams (op. cit. p. 54) subdivides domes into three broad types:

(i) Plug domes which represent upheaved conduit fillings.

(ii) Endogenous domes which grow by expansion from within.

(iii) Exogenous domes built by surface effusion, usually from a central summit crater.

One dome occurs on the Kaputar Road and intrudes Mesozoic sandstones, forming a ring-shaped structure, the central part of the dome being covered by sandstone which has not yet eroded away. The diameter is 1.5 miles, the surface is irregular, and there appear to be subsidiary

domes within the area of outcrop. This may be due to an irregular feeding conduit. A steep-sided peak occurring on top of the dome is composed of trachyte, and has platy jointing parallel to the walls of the intrusion, becoming horizontal at the top. The jointing on the top is generally undulating and seems to indicate the contours of the roof of sediments under which the trachyte was intruded. A concentric lineation is visible on aerial photographs. The absence of rubble and angular blocks on the surface, the presence of the sub-horizontal undulating platy jointing on the top surface, and the fact that few vesicles occur in the lava appears to support an intrusion of the endogenous type, as defined by Williams (1932, p. 54) i.e. an intrusion under a cover of country rocks.

Another trachyte dome, south-west of Killarney Gap, is about 1.5 miles long, 1 mile wide, and has a dome-shaped surface and an elevation above the surrounding rocks of over 500 feet. A concentric lamination is detectable from aerial photographs. In cross section, the jointing tends to be parallel to the surface of the dome on the west. In a creek which cuts through the dome on the eastern side, Permian sediments which form the floor of the dome have been indurated by the heat of the intruded lava. The trachyte of the dome, immediately above this, has rough jointing, perhaps indicating flow structure, and this jointing dips towards the centre of the dome at about 60°. The lava is not vesicular, and thus the dome was most likely injected endogenously.

Many other domes are present in the province. Some of the more bulbous types of trachyte dykes resemble domes, and a transition between

the two can be seen in various localities in the Nandewars.

The general absence of trachytic tuffs or explosion breccias indicates that the domes in the Nandewars are generally endogenous.

Williams (1932) states that perfect dome shapes are unknown because the lower slopes are covered with talus deposits, but the sides of domes would probably prove to be vertical if the lower talus were removed. If the domes are exogenous in type, the crusts of the domes tend to be shattered during extrusion, and the surface is littered with angular blocks. The expansion of the dome during emplacement presumably causes the blocky cover, and due to the rapidity of cooling jointing will usually be quite irregular, and strong columnar jointing is absent. None of these features of exogenous domes are seen in the Nandewars.

Jointing is best seen in those domes emplaced under a cover of rocks; and in these cases the jointing is dominantly vertical, and crudely concentric with the margins or radial, while there may also be platy jointing parallel to the surface, this latter simulating flow banding. Platy jointing bears no relation to the inner form of the dome. These feature of endogenous domes as described by Williams (1932) are rather similar to those found in the Nandewars, and supports the belief that the Nandewar domes are endogenous.

The lava of the endogenous domes is poor in gas, according to Williams (1932), since the highly gas-charged lavas would punch their way to the surface by volatile pressure. The paucity of gas in the endogenous types gives lavas which are not very vesicular, although they are viscous. High viscosity of lava appears to be necessary for the formation of domes, since only rhyolitic, dacitic, trachytic, and

andesitic types have been found (Williams, op. cit.). The growth of the domes is also rapid, since the lava would chill if intruded slowly.

The development of domes appears to represent the close of activity at many vents. This is particularly so for the exogenous types of domes, and the presence of highly differentiated comenditic rocks in the Nandewar domes shows that these are also late in the volcanic cycle, if the reasonable assumption that the sequence of activity has been from basic to acid, is made.

A ring structure of trachyte exists in Pound Creek, consisting of a ring dyke of trachyte with a trachyte plug as a central core. The jointing varies, but is dominantly vertical; concentric lineaments are also visible on aerial photographs. Several satellitic radial dykes are offshoots of the main mass. The grainsize of the trachyte in the structure varies, while the flow structure is random.

A minor flow of trachyte 50-100 feet thick exists to the north of Killarney Gap, while the top of Castle Top Mountain is also capped by a minor trachyte flow. Both these flows are not persistent laterally, although they are thicker than any of the basaltic flows. The Killarney Gap flow, being the most basic trachyte in the province, is somewhat more extensive than other trachyte outcrops.

Volcanic tuffs and breccias of trachytic composition are absent in the Nandewars, unlike the Warrumbungles, (Jensen, 1907). Either all the original trachytic tuffs have been eroded away, or else the trachytes were not emplaced during explosive volcanism. The latter possibility is favoured because of the non-vesicularity of the trachytes; their

texture is more appropriate to an emplacement beneath a cover of country rocks.

Great variation in mode of occurrence in the trachytes naturally leads to great difference in their textures. However the major minerals present (sometimes to the exclusion of all others) are the felspars, and some division of the trachytes on the basis of the type of felspar present seems desirable. The differentiation of the rocks at the trachytic stage of alkali enrichment of the magma is controlled by felspar fractionation.

From theoretical considerations (Tuttle and Bowen 1958; Turner and Verhoogen (1960)) and the practical results of Carmichael (1960, 1963), distinction can be drawn between two felspar trachytes (plagioclase + alkali felspar) and one felspar trachytes (alkali felspar). The former corresponds to the earlier stage of differentiation in the trachyte series; the latter represents the final stage.

Carmichael (1963) believes that only in the volcanic orogenic series of rocks, where basaltic magma is modified by assimilation to produce andesite, do the acid liquids give rise to two felspar assemblages (phenocrysts of plagioclase and alkali felspar or sanidine). The alkaline and tholeiitic series are made up of the one series of felspars - the plagioclase - anorthoclase solid solution series (op. cit. 1963). Carmichael (1963) has largely been concerned with equilibrium crystallisation.

In the Nandewar province, the crystallisation of the volcanics, in particular the trachytes, has been largely a non-equilibrium process. In some of the trachytes two or more progressive members of the plagioclase

-potash oligoclase - anorthoclase - alkali felspar differentiation series are present. On the other hand, the most differentiated trachytes and comendites consist of one felspar, a sanidine-anorthoclase cryptoperthite of the composition of the alkali felspar minimum, $Ab_{65}Or_{35}$. It is therefore necessary to distinguish these two types of trachyte, and one and two felspar trachytes, as here defined, do not correspond to those of Carmichael (1963).

Petrography

Two felspar trachytes:

The most basic trachyte in the province occurs as a minor flow near Killarney Gap (KG).

The rock has porphyritic texture, with phenocrysts of twinned oligoclase (An_{30}; albite twinning) rimmed with untwinned alkali felspar and stumpty phenocrysts of anorthoclase set in a groundmass of stumpy orthophyric felspar crystals consisting of rare oligoclase and abundant anorthoclase. Green augites, some euhedral, but most subhedral, also occur in the groundmass. Most of these augites have myriad apatite and zircon inclusions. Euhedral titanomagnetites, the larger with ilmenite exsolution laths (seen in polished section) are scattered throughout the rock. Rare phenocrysts of olivine, almost entirely pseudomorphed by sideritic carbonate, occur as phenocrysts. Measurement of a fragment of olivine which was unaltered gave an approximate $2V_{\gamma}$ of 60-80°, indicating a range of composition of from Fa_{30} to Fa_{40}.

The oligoclase phenocrysts ($\beta = 1.543$), have multiple albite twinning and are rimmed with untwinned alkali felspar; some oligoclases have exsolution of alkali felspar. Apatite and zircon inclusions are common. The anorthoclase phenocrysts ($\beta = 1.534$, $\gamma = 1.540$, $2V = 41\text{-}56°$) sometimes develop cross-hatched twinning and are rimmed with untwinned alkali felspar. Other anorthoclase phenocrysts develop 'blotchy' extinction effects, indicating transitional thermal states. Some exsolution of an unidentified felspar can also be seen. These phenocrysts are rimmed also with an untwinned alkali felspar, and some have a rim of inclusions near the margin of the crystals.

The groundmass felspars consist of rather sparse stumpy oligoclase crystals together with abundant anorthoclase.

Trachyte 22 is similar to the one just described from Killarney Gap, and consists of phenocrysts of anorthoclase, oligoclase, and subhedral green augites ($\beta = 1.716$, $2V = 55^{\circ}$) set in a groundmass of anorthoclase and rare oligoclase.

Another two felspar trachyte (151-2) has phenocrysts of anorthoclase ($\alpha = 1.529$, $\beta = 1.536$, $\gamma = 1.540$, $2V = 41\text{-}55^{\circ}$) and oligoclase (extinction angle $11\text{-}12^{\circ}$), both types of felspar being rimmed with alkali felspar with $\beta = 1.525$. The groundmass felspar laths, with trachytic flow structure, consist of alkali felspar with $\alpha = 1.526\text{-}1.528$. Some phenocrysts of green augite $\beta = 1.720$, $2V = 56^{\circ}$ are also present, as well as titanomagnetites.

These two felspar trachytes are the most basic types, and are transitional to mugearite (Muir and Tilley, 1961).

<u>One felspar trachytes</u>:

All the other trachytes possess one felspar alone, a member of the sanidine - anorthoclase cryptoperthite series (Tuttle, 1952) trending towards the final composition $Or_{35}\ Ab_{65}$, a minimum on the Or - Ab join.

The trachyte 24 from a dome on the Kaputar road, is typical. It consists of phenocrysts of alkali felspar ($\beta = 1.531$, $2V = 56\text{-}60^{\circ}$) set in a trachytic groundmass of alkali felspar laths with interstitial green aegerine-augite ($\beta = 1.758$, $2V = 88^{\circ}$), arfvedsonite (X = dark blue green, Y = pale violet brown, Z = dark green, $2V = 71^{\circ}$) and cossyrite (X = light brown, Z = Y = dark brown), with some interstitial

quartz also, and titanomagnetite (some rimmed with cossyrite).

The trachytes occurring on the Governor (e.g. GOV4) are similar, consisting of alkali felspar phenocrysts ($\alpha = 1.526$, $\beta = 1.532$, $\gamma = 1.534$, $2V = 60\text{-}61^{\circ}$), green sodic ferrohedenbergite phenocrysts ($\alpha = 1.722$, $\beta = 1.734$, $\gamma = 1.756$, $2V = 66^{\circ}$, analysis GOV4px) set in a groundmass of elongate sodic ferrohedenbergites, laths of alkali felspar with trachytic flow structure, and interstitial arfvedsonite and cossyrite. There are sparse titanomagnetite crystals, often rimmed with cossyrite.

In one of the trachytes on the Governor (GOV2) the only ferromagnesian minerals present are aegerine-augite and titanomagnetite. This difference in the ferromagnesian assemblage in otherwise similar rocks is held to be due to differences in P_{O_2}, and this will be discussed later. In another of the trachytes from the Governor (GOV1) the cossyrite shows a peculiar pleochroism of dark green to red brown.

In several of the trachytes from Castle Top Mountain (CT1, CT2), generally similar assemblages are present, but the amphibole has quite distinct optics, with a pleochroic scheme : X = light brown-green; Y = dark brown-green; Z = dark yellow-green, $X < Y < Z$, $Z'c = 23^{\circ}$. The amphibole does not appear to be similar to the bluish riebeckite-arfvedsonites found elsewhere, and is probably quite distinct in composition.

In the more differentiated trachytes (100-6, Mt. W), a fine grained mass of carlsbad twinned alkali felspar and poikilitic riebeckite-arfvedsonites are present, together with interstitial quartz. In the

Mt. W. trachyte there are also some phenocrysts of alkali felspar ($2V = 50-58^{\circ}$), and also abundant small zircons in the groundmass.

An alkali syenite (118-2) has been found in Oakey Creek, with phenocrysts of oligoclase with multiple albite twinning ($\alpha = 1.545$, $\gamma = 1.555$, An_{33-35}), mauve titanaugite ($\alpha = 1.693$, $\beta = 1.699$, $\gamma = 1.718$) set in a groundmass of alkali felspar and quartz. This rock is the coarse grained equivalent of the trachytes. There is extensive carbonate alteration.

Comendites:

In the final stage of differentiation, only alkali felspars and quartz are present. These rocks usually have a molecular excess of $Na_2O + K_2O$ over Al_2O_3, and are termed comendites. (Lacroix, 1930) Jensen (1907) has called these rocks bostonites.

These comendites (73-12, 73-5, 104-E, Mt. L, 26) consist of phenocrysts of sanidine-anorthoclase cryptoperthite ($\alpha = 1.526-1.528$, $\beta = 1.532$, $\gamma = 1.533-1.535$, $2V = 42-59^{\circ}$) which often have blotchy extinction and minor exsolution, set in a groundmass of alkali felspar laths with trachytic flow structure and simple Carlsbad twinning, together with interstitial quartz. The comendite 73-12 has orthophyric texture, with the felspar phenocrysts set in a mass of stumpy anorthoclase laths with interstitial quartz.

These comendites have compositions trending towards the minimum melting composition in the system $NaAlSi_3O_8 - KAlSi_3O_8 - SiO_2$; with felspar of composition $Ab_{65}Or_{35}$ and quartz.

MINERALOGY OF THE ALKALINE ROCKS

OLIVINES

The most conspicuous feature of the Nandewar alkaline volcanic province is the paucity of olivine basalts, which are normally the most abundant rock type in alkaline provinces of the oceanic islands such as Hawaii, (Macdonald, 1949), Tahiti (Williams, 1933), Samoa (Macdonald, 1944), St. Helena (Daly, 1927) and Gough Island (Le Maitre, 1962). An abundance of olivine basalts is also common in continental alkaline provinces; in Victoria (Edwards, 1938a and 1938b) and in the Otago province, New Zealand (Benson, 1941).

In the few flows of olivine basalt which do occur in the Nandewars, the olivine forms phenocrysts, often altered along the rims and cracks within the mineral grains, to "iddingsite" (see discussion in the teschenite section on the validity of this mineral) and serpentine minerals. In the trachyte KG only small residual of olivine, within the core of a sideritic carbonate pseudomorph, was found. The uncertainty of the optical determination of this grain naturally leads to a similar uncertainty in the composition, but the value Fa_{40} is favoured rather than Fa_{30} on chemical grounds (the Fe/Fe + Mg ratio of the ferromagnesian minerals in the norm is 47.6).

All the olivine compositions have been determined optically using the graph of Deer, Howie, and Zussman (1962, vol. 1, p. 22, Fig. 11), which was compiled in part from Bowen and Schairer (1935). The olivine optics, compositions, and Fe^{2+}/Fe^{2+} + Mg ratios in the ferromagnesian minerals of the norms of the rocks from which they were taken, are set out in Table 8 .

The iron-rich nature of the olivine, its paucity, and also the low MgO contents of the rocks themselves, attests to the relatively differentiated nature of even the most basic olivine basalt in the volcanic phase (Gr 1).

In the table it can be seen that, for the analysed rocks, the olivine is more Fe^{2+} rich than the corresponding Fe^{2+}/Fe^{2+} + Mg ratio in the ferromagnesian minerals of the norm. This is caused by oxidation and alteration of the analysed rocks, and is a petrogenetic point which will be discussed later.

Where both olivine and clinopyroxene are present (e.g. in the analysed rocks 5P and KG, and the analysed clinopyroxenes from them; and also in the olivine basalt Gr1), the olivine is enriched in Fe^{2+} relative to the clinopyroxene (Fig. 1), the relation usually seen in alkaline rocks (Muir and Tilley, 1961; Le Maitre, 1962; Aoki, 1964; Carmichael, 1960a, and Wilkinson, 1958). Unlike these quoted examples, however, the Nandewar province does not show any examples of olivines persisting beyond the middle stage of differentiation, where a composition of Fa_{40} is attained.

TABLE 8

SOME OPTICAL PROPERTIES OF OLIVINE IN NANDEWAR ROCKS

Rock number and type		Optics	Composition	Ratio Fe^{2+}/Fe^{2+} + Mg in norm ferromag.
CT6	porphyritic olivine basalt	β1.699	Fa_{23}	
32	" " "	β1.700	Fa_{24}	
5	" " "	α1.684 γ1.723	Fa_{27}	
5P	" " "	β1.698	Fa_{23}	11.8
Gr 1	" " "	β1.704	Fa_{26}	16.7
E7	" " "	β1.717	Fa_{31}	19.4
E8	" " "	β1.722	Fa_{34}	23.9
KG	trachyte (two felspar)	$2V^{-}=60-80^{\circ}$	Fa_{30-40}	47.6

Refractive indices accurate to ± 0.002

The rocks 5P, Gr 1, E7, E8 and KG have been chemically analysed (Tables29-32).

PYROXENES

General Statement and Separation methods:

Pyroxenes are present in all the alkaline rocks examined except the leucocratic comendites, which have no ferromagnesian minerals at all.

Separation methods varied for the different pyroxenes. The pyroxene xenocryst Plpx was dug directly out of the rock, crushed to pass 100 mesh, centrifuged in methylene iodide and cleaned by treating in a 1:1 HCl solution over a water bath, for 4 hours, extracted with a 10 per cent solution of Na_2CO_3 (Muir and Tilley, 1961, p. 193), and finally centrifuged in methylene iodide. The acid treatment removes any magnetite and olivine, while the extraction in Na_2CO_3 removes any gelatinous silica (Muir and Tilley, loc. cit.). For the pyroxenes 5Ppx and GOV4px the 100-150 mesh fraction of the rock powder was used, and initial separation of the heavy fraction was made in a separating funnel with methylene iodide. This was done in order to remove the groundmass pyroxene, which because of its fine grainsize, was floated off in composite felspar-pyroxene grains. The subsequent separation procedure followed that already outlined. For the groundmass pyroxene 10px, a fine fraction was used for the separation (200 to 250 mesh).

Clinopyroxene xenocryst:

The diopside xenocrysts from the analcitite are large (up to 1" long) and have extensively developed marginal reaction zones with the analcitite magma. There are two varieties of pyroxene xenocrysts : a titanaugite which is dark lustrous black in hand specimen, and diopsidic augite, which is somewhat lighter coloured in hand specimen. The titanaugite is

pale mauve in thin section, whereas the diopside is pale green. Similar pyroxene xenocrysts have been observed by Walker and Ross (1954) from a xenolithic monchiquite dyke. The pyroxene analysed here is from a titanaugite xenocryst. Both the green diopsidic augite and mauve titanaugite have deeper mauve titanaugite reaction rims, and these are more fully described in the section on analcitite. The dispersion of the titanaugite xenocryst is notably very high, (r v) indicating large amounts of Tschermak's component (Ca, Mg) $AlAlSiO_6$, (Deer, Howie, and Zussman, 1963 vol. 2, p. 165, and Lovering and White 1964, p. 202). The crystals commonly do not go to complete extinction in white light.

Clinopyroxenes from olivine basalts to trachytes:

The porphyritic olivine basalts have large mauve phenocrysts of titanaugite and smaller euhedral crystals of augite in the groundmass. The phenocrysts are sometimes zoned, are generally euhedral, and often possess twinning parallel to (100). In several of the olivine basalts the titanaugite phenocrysts suffer reaction on the margins of the crystals where there are myriad small magnetites.

The fine grained trachyandesites contain uniformly small euhedral clinopyroxenes showing no alteration. The pyroxene from the trachyandesite 10 is an example of this type. The fine grainsize made it difficult to concentrate a pure sample of the pyroxene, and the analysis has been recalculated to account for small amounts of plagioclase impurity. This has been done by subtracting plagioclase of the composition of that in the norm of the rock as a whole ($Or_{17}Ab_{50}An_{33}$), and recalculating the

analysis to 100 per cent.

The pyroxene separated from the Killarney Gap trachyte, the most basic trachyte in the province, is pale green, forms euhedral to subhedral crystals, and contains many apatite and zircon inclusions. In some places, the pyroxene has crystallised entirely within felspar phenocrysts, and is preferentially elongated along cleavage planes of the felspar. The acid treatment of the pyroxene would have removed most of the apatite, but the high content of P_2O_5 in the analysis shows that some apatite remained.

The pyroxenes from trachytes 22 and 151-2 have been studied optically, and they resemble the Killarney Gap trachyte pyroxene in many respects, although the crystals tend to be more anhedral and occur interstitially between the felspar laths. Their optics (corrected) show them to have similar compositions to the pyroxene from KG.

The analysed pyroxene from the trachyte GOV4 forms phenocrysts which are mid-green, euhedral (sometimes elongated parallel to c), and often have narrow darker green rims indicating a progressive reaction with the magma. There are many anhedral greener pyroxene crystals in the groundmass, and these appear to be somewhat richer in acmite than the phenocrysts, having lower extinction angles and higher birefringence.

In other trachytes (e.g. 24) the pyroxene forms green interstitial crystals with a high birefringence, low extinction angles, and high 2V values. The optics of the pyroxene from 24 indicate enrichment in the acmite component, the estimated composition being about $Ac_{50}He_{50}$. Unfortunately, it was impossible to separate the pyroxene for analysis due to its fine grainsize and intimate association with both cossyrite and arfvedsonite.

TABLE 9

SOME OPTICAL PROPERTIES OF CLINOPYROXENES FROM ROCKS NOT ANALYSED

Rock No.		α	β	γ	$2V_\gamma$	Remarks
1	porphyritic basalt	1.697	1.706	1.723		Titanaugite phenocrysts with euhedral groundmass augites
5	porphyritic olivine basalt		1.697			" " "
32	porphyritic olivine basalt	1.701	1.705			" " "
CT6	porphyritic olivine basalt		1.701			" " "
7	trachyandesite		1.703			" " "
9	trachyandesite		1.706			" " "
18	trachyte		1.737			Green aegerine-augite phenocrysts
22	trachyte		1.716		55°	Green augite crystals
CT1	trachyte	1.708	1.730			Green aegerine-augite crystals.

Rock numbers 1, 5, 7, 9, 18, 22 collected from Kaputar Road, to the west of Coryah Gap.

Rock numbers CT1, CT6 collected from Castle Top Mountain, from the summit, and half way down the mountain respectively.

TABLE 10

SOME OPTICAL PROPERTIES OF THE CLINOPYROXENES FROM THE ANALYSED ROCKS

Rock No.		α	β	γ	$2V_\gamma$	$\gamma \wedge c$	Remarks
CTS	contact teschenite		1.698				Euhedral purple zoned crystals
E7	porphyritic basalt	1.701	1.709				Euhedral groundmass augites with titanaugite phenocrysts
"5P	porphyritic olivine basalt	1.703	1.707	1.727	53°		" " "
GR1	porphyritic olivine basalt		1.697		56°		" " "
"10	trachyandesite						Euhedral augites in groundmass
15	trachyandesite						" " "
E8	porphyritic basalt		1.695				Titanaugite phenocrysts with euhedral groundmass augites
8A	trachyandesite						Very fine grained euhedral groundmass augites
118-2	Alkali syenite	1.693	1.699	1.718			Titanaugites
"KG	trachyte	1.708	1.714	1.731	50°	42°	Greenish augites
151-2	trachyte	1.708	1.718	1.732	56°	42°	" " "
24	trachyte		1.758		88° ($2V_\alpha$)	5°	Green interstitial aegerine-augites
"GOV4	trachyte	1.722	1.734	1.756	66°	41°	Green ferrohedenbergite phenocrysts with groundmass hedenbergites

" Analysed pyroxenes

Chemistry:

The formula of pyroxenes is usually written as follows (Berman, 1937; Hess, 1949; Kuno, 1955):

$$(W)_{1-p}\ (X,Y)_{1+p}\ Z_2O_6$$

where: $W = Ca^{2+}, Na^{+}, K^{+}$.

$X = Mg^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}$.

$Y = Al^{3+}, Fe^{3+}, Cr^{3+}, Ti^{4+}$.

$Z = Si^{4+}, Al^{3+}$.

W, X and Y are in octahedral positions (co-ordination number 6), whereas Z cations are in tetrahedral positions (co-ordination number 4).

The structural formulae of the pyroxenes have been calculated on the basis of 6 oxygens per unit formula cell, and the Z sites have been made equal to 2 by adding Al to the Si where necessary. The method of Hess (1949) of balancing the charges in calculating the formula, has not been used. Bown (1964) has criticised Hess's procedure for calculating pyroxene analyses. Bown states that:

1. The method of calculating is unecessarily complicated, leading to arithmetical errors.
2. Overall charge balance will naturally be achieved if an analysis is cast as oxides, and local charge balance as envisaged by Hess, is unlikely to be achieved in practice, especially in quickly cooled igneous rock pyroxenes.
3. All the errors in recalculation and analysis are concentrated

TABLE 11

ANALYSES AND OPTICAL PROPERTIES OF THE PYROXENES

	P1px	5Ppx	10px	KGpx	GOV4px
SiO_2	49.39	49.46	52.91	52.49	49.14
TiO_2	1.57	3.57	2.66	0.84	0.59
Al_2O_3	7.75	4.26	1.26	1.90	0.93
Fe_2O_3	3.06	2.17	2.75	2.28	4.04
FeO	4.20	7.37	6.96	13.42	24.14
MnO	0.13	0.15	0.27	0.67	1.06
MgO	13.41	13.40	14.13	9.68	0.90
CaO	18.12	19.65	17.34	17.77	18.29
Na_2O	1.53	0.66	0.81	0.74	1.17
K_2O	0.02	0.01	0.91	0.19	0.17
P_2O_5	0.08	tr	tr	0.12	tr
H_2O^+					
H_2O^-					
Total:	99.26	100.70	100.00	100.10	100.43
α		1.703		1.708	1.722
β	1.693	1.707		1.714	1.734
γ		1.727		1.731	1.756
$2V_\gamma$	60°	52°		50°	66°
γ^c				42°	41°
Disp.	r≫v high	r>v mod.			
Colour	pale mauve	mauve	very pale mauve	pale green	mid-green

P1px: Clinopyroxene xenocryst from analcitite with ultrabasic xenoliths, Dingo Creek.
5Ppx: Titanaugite phenocrysts from olivine basalt 5P, Kaputar Road.
10px: Groundmass clinopyroxene from trachyandesite 10, Kaputar Road.
KGpx: Augite from trachyte KG, Killarney Gap.
GOV4px: Hedenbergite phenocrysts from trachyte GOV4, summit of the Governor.

TABLE 12

STRUCTURAL FORMULAE OF THE PYROXENES CALCULATED ON THE BASIS OF 6 OXYGENS --- XYZ_2O_6

	P1px		5Ppx		10px		KGpx		GOV4px	
Si	1.844	2.000	1.829	2.000	1.957	2.000	2.000		1.982	2.000
Al^{IV}	0.156		0.171		0.043				0.018	
Al^{VI}	0.185	2.033	0.014	1.969	0.012	1.953	0.085	1.940	0.026	1.964
Ti	0.044		0.099		0.074		0.024		0.018	
Fe^{3+}	0.086		0.060		0.077		0.065		0.126	
Mg	0.746		0.737		0.779		0.549		0.054	
Fe^{2+}	0.131		0.228		0.215		0.427		0.814	
Mn	0.004		0.005		0.008		0.002		0.036	
Ca	0.725		0.778		0.687		0.724		0.790	
Na	0.111		0.047		0.058		0.055		0.091	
K	0.001		0.001		0.043		0.009		0.009	
per cent Al in Z	7.8		8.6		2.2		0		0.9	
Mg	44.1		40.8		44.1		31.1		3.0	
ΣFe	13.1		16.2		17.0		28.0		53.6	
Ca	42.8		43.0		38.9		40.9		43.4	
Mg	77.5		72.5		72.2		52.7		5.6	
Fe^{2+}	13.7		22.5		20.0		41.0		84.0	
$NaFe^{3+}$	8.8		5.0		7.8		6.3		10.4	
Ac	8									
Jd	3									
Ts	17									
Hd	14									
Di	58									

$\Sigma Fe = Fe^{2+} + Fe^{3+} + Mn$

in the last stage of Hess's procedure, whereas if Z is made equal to 2, or if Z is made equal to Y, the errors are evenly distributed.

4. The Hess recalculation often gives a substantially different distribution of Al between Y and Z sites, when compared to the two other methods outlined in 3.

It has not been found necessary to place any Ti in tetrahedral sites (Wilkinson, 1957a; Carmichael, 1960), because of the relative abundance of Al, amply sufficient to satisfy requirements in each case.

The analyses of the series of pyroxenes shows that silica rises in the middle of the differentiation sequence (the groundmass pyroxene from trachyandesite 10, and the pyroxene from the Killarney Gap trachyte KG both have silica in the range 52-53 per cent as opposed to 49 per cent for the other pyroxenes). This higher value of silica is related to slightly lower CaO in each case.

The titanium is high, as expected in the Mg-rich titanaugites, but decreases as the pyroxenes differentiate towards hedenbergite. The TiO_2 of the xenocryst diopside from the analcitite is lower than that in the titanaugite phenocryst from the olivine basalt 5P, even though the latter is poorer in MgO. The diopside phenocryst is pale mauve, but has deeper mauve reaction rims, and it appears that the Ti increases in these rims.

The Al_2O_3 is high in the diopside xenocryst from the analcitite (7 per cent), and falls rapidly in more differentiated pyroxenes in the series, and the proportion of Al in Z sites also decreases rapidly

(Le Bas, 1962).

MgO and FeO are antipathetically related, while the Ca content remains constant, and high, throughout. Most of the total iron occurs as FeO, and there is but minor enrichment in the acmite molecule in the analysed pyroxenes.

The sodium is high in the diopside xenocryst, and calculates out as acmite + jadeite. The sodium content of the titanaugite phenocryst, from 5P, is much lower, but sodium rises, reaching a maximum of 1.17 per cent in the pyroxene from the trachyte GOV4. In each case, except pyroxene P1, and the groundmass pyroxene from the trachyandesite 10, Na + K is slightly smaller in the formula than Fe^{3+}. In the two cases where it is not, Al^{3+} combines with Na + K, and forms jadeite.

Optics:

Wilkinson (1957a), and Le Maitre (1962) have shown that, except in a general way, optical properties of the clinopyroxenes cannot be correlated with the chemistry using the graphs of Hess (1949), and Muir (1951). Hori (1954) has suggested that Al, Ti, and Fe^{3+} in tetrahedral co-ordination increase the optic axial angle and lower the β refractive index, whereas in octahedral sites these ions have the opposite effect.

The measured 2V values and β refractive indices of the analysed pyroxenes are compared with values read of the graph of Hess (1949), modified by Muir (1951), in Deer, Howie and Zussman (1963, vol. 3, p. 132), in Table 13 . Carmichael's (1960) amended values for hedenbergite rich compositions are also shown for the pyroxene phenocrysts from trachyte

TABLE 13

COMPARISON OF OPTICAL PROPERTIES MEASURED ON THE ANALYSED PYROXENES AND VALUES PREDICTED FROM THE GRAPH OF HESS (1949) MODIFIED BY MUIR (1951), AND FIGURED BY DEER, HOWIE, AND ZUSSMAN (1963, vol. 3, p. 132), AND ALSO FROM CARMICHAEL, (1960, p. 322).

Pyroxene	Measured values		Predicted values	
	2V	β	2V	β
P1	60°	1.693	52°	1.687
5P	53°	1.707	53°	1.690
K.G.	50°	1.714	50°	1.705
GOV4	66°	1.734	58°	1.735
			(from Carmichael, 1960)	
			56°	1.743

GOV4.

The composition - optics curves of Hess (1949) were drawn up on the assumption of 3 per cent Al_2O_3 ; Fe_2O_3 1.5 per cent ; Na_2O 0.4 per cent ; TiO_2 0.4 per cent ; MnO 0.3 per cent and negligible Cr_2O_3 for the range of clinopyroxene compositions in the present analyses.

For the diopside xenocryst P1 from the analcitite, the 2V is smaller by 8° and the β refractive index larger by 0.006 than indicated by the graph in Deer, Howie, and Zussman (loc. cit.). According to Hori (1954) this can be explained by the effect of Fe^{3+}, Ti and Al (in octahedral co-ordination) on the optics, especially on the 2V. For the titanaugite phenocrysts from the olivine basalt 5P the measured 2V is the same as that predicted by the graph, while the measured β refractive index is 0.017 larger. Presumably the effect of Fe^{3+}, Ti and Al in octahedral co-ordination is partly counterbalanced by the rather high amount of Al in the Z group. This gives a similar 2V, with a slightly higher β index. The augite phenocrysts from the trachyte K.G. have the same 2V as predicted from the graph, but a slightly higher β index, which can be ascribed to both the Fe^{3+}, Ti and Al in octahedral co-ordination as well as to the effect on the optics of the acmite component. With the hedenbergite phenocrysts from the trachyte GOV4, the measured 2V is much higher than that on the graphs of both Deer, Howie, and Zussman (loc. cit.) and Carmichael (1960, p. 322) due to the effect of the acmite component.

Applying a similar correction to the 2V values and β refractive indices of the pyroxene phenocrysts from the trachytes 151-2 and 22 as

to that of the trachyte pyroxene phenocrysts from K.G. (i.e. lowering the β refractive index by about 0.009) shows that they have quite a similar composition to the pyroxene of trachyte K.G.

The caution expressed by many workers in determining compositions of Ca rich clinopyroxenes (Brown, 1957; Carmichael, 1960; Wilkinson, 1957a; Murray, 1954) from optical properties alone is well justified unless one draws up a different graph for each type or series of speciments - a graph for Skaergaard type pyroxenes (Muir, 1951; Brown, 1957), a graph for pitchstone type pyroxenes (Carmichael, 1960), one for pyroxenes from undersaturated alkaline trends (Murray, 1954; Wilkinson, 1957a) and another for saturated - oversaturated alkaline trends, as exemplified by this study, and so on.

Crystallisation trends:

The analysed pyroxenes have been recalculated as atomic percentages of Ca, Fe, and Mg (where $Fe = Fe^{2+} + Fe^{3+} + Mn$); and also as atomic percentages of Fe^{2+}, Mg, and $NaFe^{3+}$ (any excess of Fe^{3+} over Na + K is usually placed with the Fe^{2+}, Carmichael, 1962). These recalculated compositions have been plotted on the Di-He-Fs-En quadrilateral (Fig. 1), and on the Na + K, Fe^{2+}, Mg triangle (Fig. 2). This latter triangle represents a plane in the En-Fs-Wo-Ac tetrahedron as shown in the inset (af. Carmichael, 1962, p. 94, Fig. 2), and is one which slopes from the 40 per cent Wo line in the Wo-En-Fs triangle to the Ac apex of the tetrahedron.

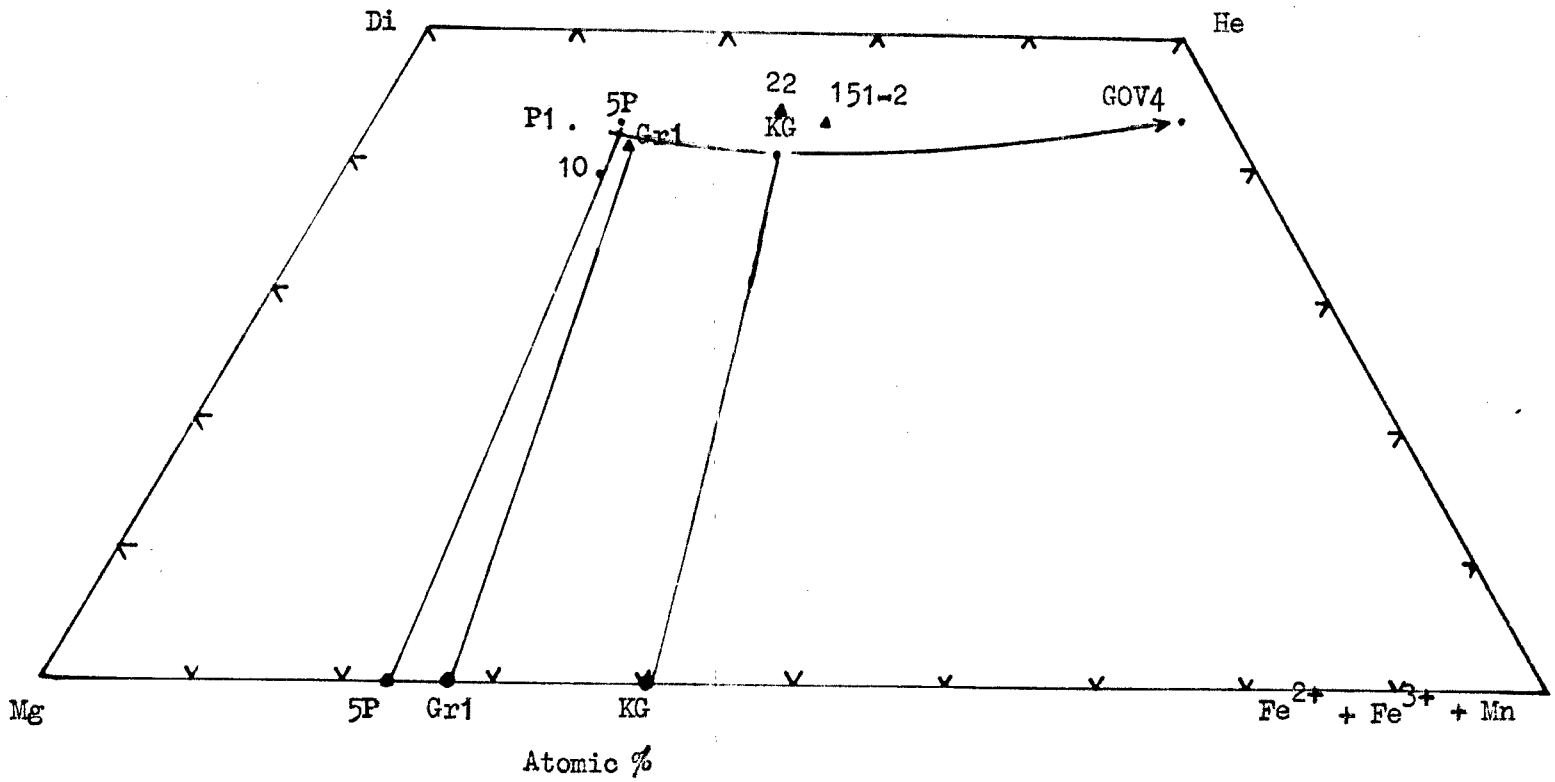

Figure 1

Plot of analysed clinopyroxenes (small circles), also optically determined climopyroxenes (triangles) with tie-lines to co-existing olivines (large circles).

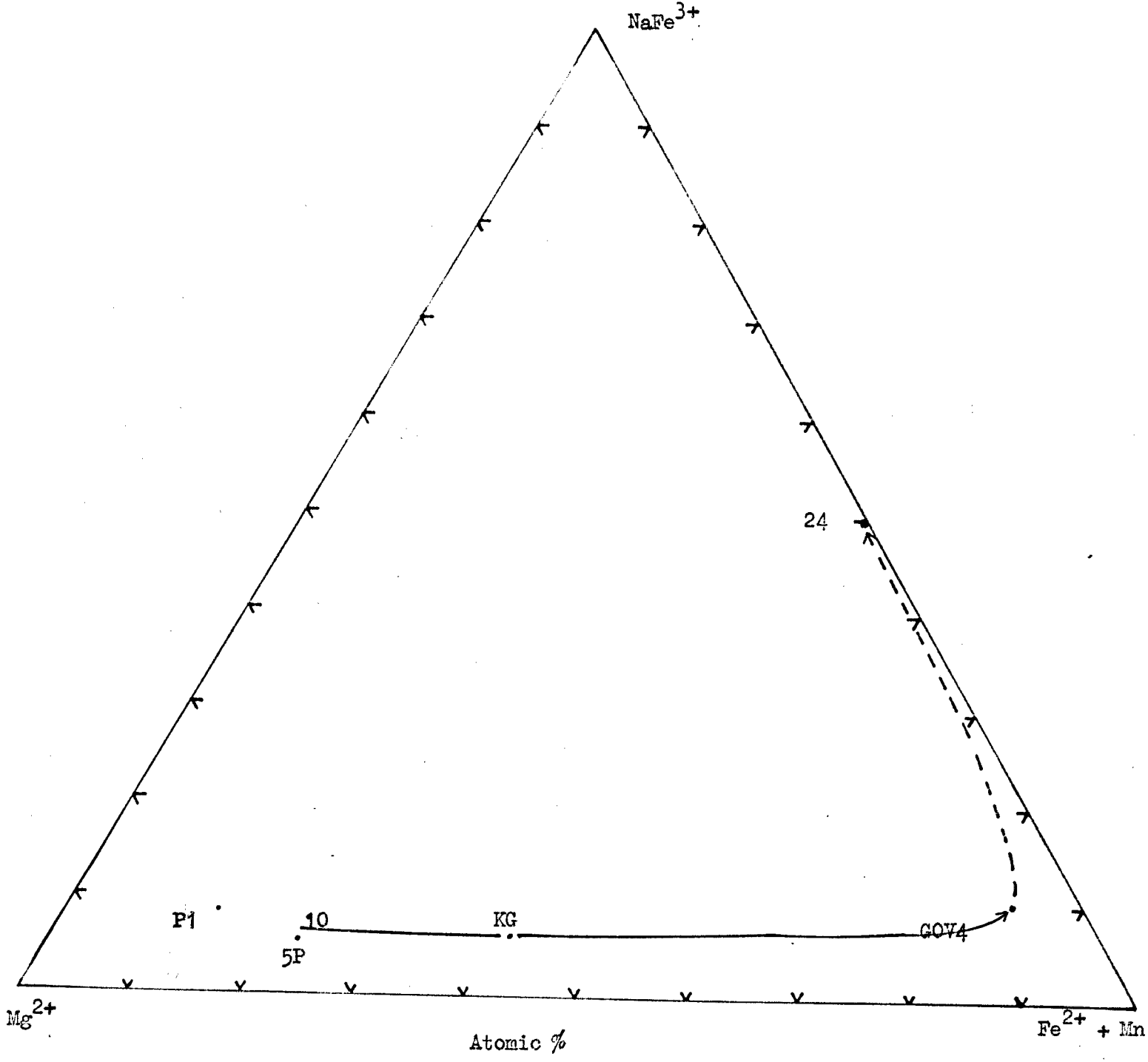

Figure 2

Plot of analysed clinopyroxenes in the system Di-He-Ac, together with optically determined clinopyroxene from trachyte 24.

Clinopyroxene xenocryst:

The pyroxene xenocryst P1 from the analcitite contains considerable amounts of alumina and sodium which take its composition outside the plane Di-He-Fs-En. White (1964) has discussed the pyroxenes from basic granulites and eclogites, and has distinguished them on the basis of the partition of Al between tetrahedral and octahedral sites in the lattice.

The pyroxene analysis P1, after calculating the structural formula on the basis of 6 oxygens (XYZ_2O_6), is recast into hypothetical and member molecules Ac, Jd, Ts, Hd and Di according to the procedure of Yoder and Tilley (1962), except that all Fe^{3+} in the Y sites is combined with Na + K to form acmite, and the remaining Na + K (if any) is combined with an equal amount of Al in the Y sites to form jadeite (White, 1964, p. 884), where:

Ac = acmite, $NaFe^{3+}Si_2O_6$.

Jd = jadeite, $NaAlSi_2O_6$.

Ts = Tschermak's component, $(Ca,Mg)Al^{VI}Al^{IV}SiO_6$.

Hd = hedenbergite, $CaFe^{2+}Si_2O_6$.

Di = diopside, $CaMgSi_2O_6$.

It has been found necessary for the pyroxene P1 to place the Ti in with the Ts, even though this procedure leads to charge imbalance. Kushiro and Kuno (1963) have postulated a Ca-Ti "pyroxene", $CaTiAl_2O_6$,

TABLE 14

COMPARISON OF CLINOPYROXENE XENOCRYSTS ANALYSED FROM THE ANALCITITE WITH ULTRABASIC XENOLITHS, DINGO CREEK, NANDEWARS.

	3.	Plpx
SiO_2	47.91	49.39
TiO_2	1.39	1.57
Al_2O_3	5.45	7.75
Fe_2O_3	3.91	3.06
FeO	6.64	4.20
MnO	0.21	0.13
MgO	11.23	13.41
CaO	19.95	18.12
Na_2O	1.70	1.53
K_2O	0.04	0.02
H_2O^+	0.45	
H_2O^-	0.20	
CO_2	0.97	
P_2O_5		0.08
Cr_2O_3	tr	
NiO	tr	
Total	100.05	99.26
α	1.706	
β	1.712	1.693
γ	1.733	
$2V_\gamma$	60°	

Structural formulae on the basis of 6 oxygens XYZ_2O_6

	3		Plpx	
Si	1.841	2.000	1.844	2.000
Al^{IV}	0.159		0.156	
Al^{VI}	0.088	2.003	0.185	2.033
Ti	0.040		0.044	
Fe^{3+}	0.113		0.086	
Fe^{2+}	0.213		0.131	
Mg	0.643		0.746	
Mn	0.007		0.004	
Na	0.127		0.111	
K	0.002		0.001	
Ca	0.770		0.725	
Ca	45.5		42.8	
Mg	36.8		44.1	
Fe	17.7		13.1	
Ac	11		8	
Jd	2		3	
Ts	13		17	
He	21		14	
Di	53		58	

Plpx — Clinopyroxene xenocryst from Dingo Creek analcitite, analyst M.J. Abbott

3 — Clinopyroxene xenocryst from Dingo Creek analcitite, from Wilshire and Binns (1961, Tables 4a and 4b, No. 3).

in the calculation of their "mantle norm", and this could be regarded as Ti Tschermak's component.

When the above calculations are made, it is found that eclogite facies clinopyroxenes have Jd/Ts > 4/5, whereas granulite facies clinopyroxenes have Jd/Ts < 1/2. (White, 1964). When the values for the pyroxene xenocryst P1 (Jd 3 per cent, Tsch 17 per cent) are plotted on White's diagram (op. cit., p. 886), this thesis, Fig. 3 ; it is found that it plots well within the granulite field.

Wilshire and Binns (1961) have also analysed a clinopyroxene xenocryst from the analcitite sill, and their analysis (op. cit., p. 198-199, Tables 4a, and 4b., No. 3) is set out beside the present author's (Table 14). Wilshire and Binn's analysis has lower Al and higher Fe, and the recalculated analysis reveals lower Ts, but also lower Jd, so that it still plots within White's granulite field (Fig. 3).

From these analyses it can be deduced that the region of either the lower crust or upper mantle from which these xenocrysts were derived has not attained the eclogite facies.

This pyroxene P1 has also been plotted on the Di-He-Fs-En diagram (Fig.1) together with the other Nandewar analysed pyroxenes. It falls on the Mg rich end of the trend.

Olivine basalt - trachyte clinopyroxene trend:

The main trend revealed by the analysed clinopyroxenes in the Nandewars is replacement of Mg by Fe^{2+}, while the Ca content remains almost constant, falling slightly where Fe^{2+} approximately equals Mg (KGpx),

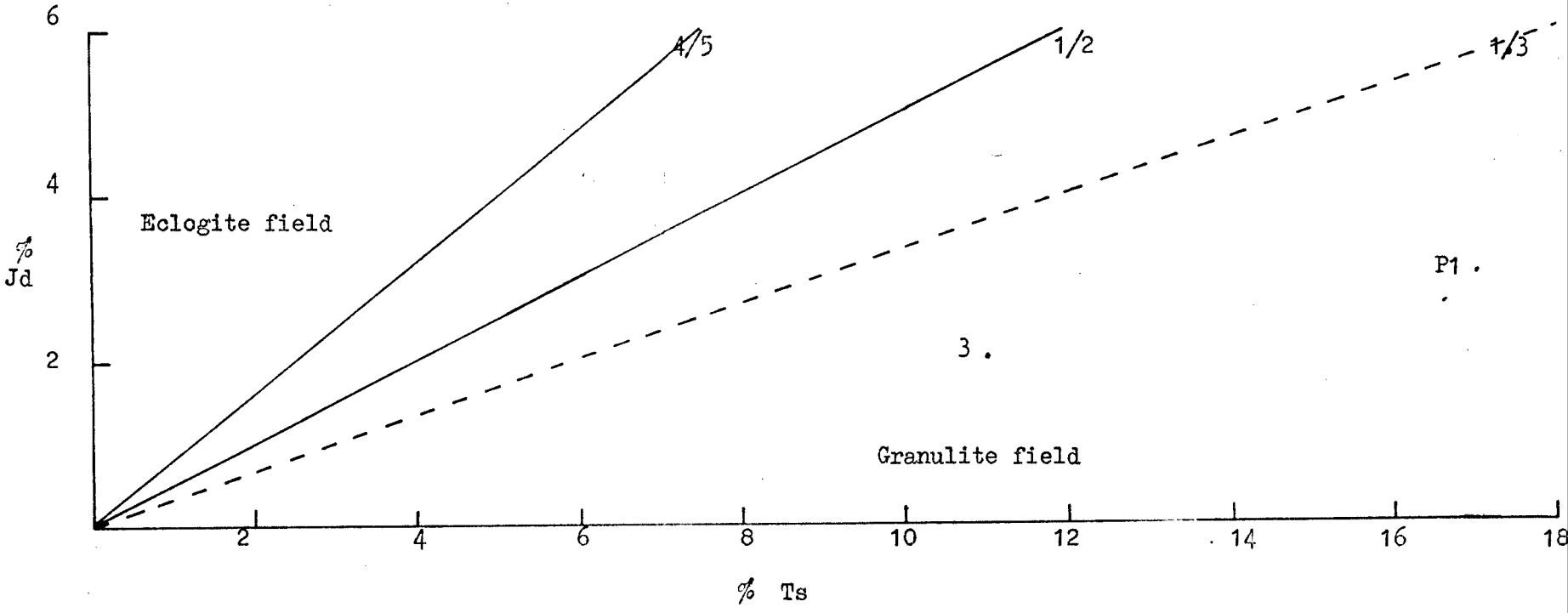

Figure 3

Plot of clinopyroxenes from analcitite on diagram after White (1964).

see Fig 1 . Only in the latest interstitial pyroxenes does the Ca fall, and the acmite molecule increase rapidly in amount (clinopyroxene from 24, $He_{50}Ac_{50}$ from optical properties); this occurs after the clinopyroxenes have reached sodic ferrohedenbergite composition (GOV4px), whereupon the trend turns sharply towards acmite, proceeding away from He along the He-Ac join.

The clinopyroxene differentiation trends from other rock series have been plotted for comparison with this study (Fig. 4). Sources of the data are: Black Jack teschenite pyroxenes, Wilkinson (1957a); Garbh Eilean pyroxenes, Murray (1954); Gough Island pyroxenes, Le Maitre (1962); Japanese alkali rock pyroxenes, Aoki (1964); Red Hill dolerite pyroxenes, McDougall (1961); Tertiary British and Icelandic porphyritic acid glass pyroxenes, Carmichael (1960); and the Skaergaard pyroxenes, Muir (1951), Brown (1957), and Brown and Vincent (1963). For soda-rich pyroxenes the trends have also been drawn in the Ac-He-Di field (Fig. 5), and the following have been inserted for comparison: Morotu dolerite - monzonite-syenite pyroxenes, Yagi (1953); sodic ferrohedenbergite pantellerite phenocrysts, Carmichael (1962); and the Black Jack, Garbh Eilean and porphyritic acid pitchstone pyroxenes, taken from Carmichael (1962, p.94). On this diagram (Fig. 5) the fields of Na-rich clinopyroxenes and Ca-rich clinopyroxenes have been drawn after Aoki (1964, p.1210, Fig. 3). According to Aoki there is little subsolvus solid solution between these two fields of composition.

In the Di-He-Fs-En quadrilateral, the Nandewar clinopyroxene trend

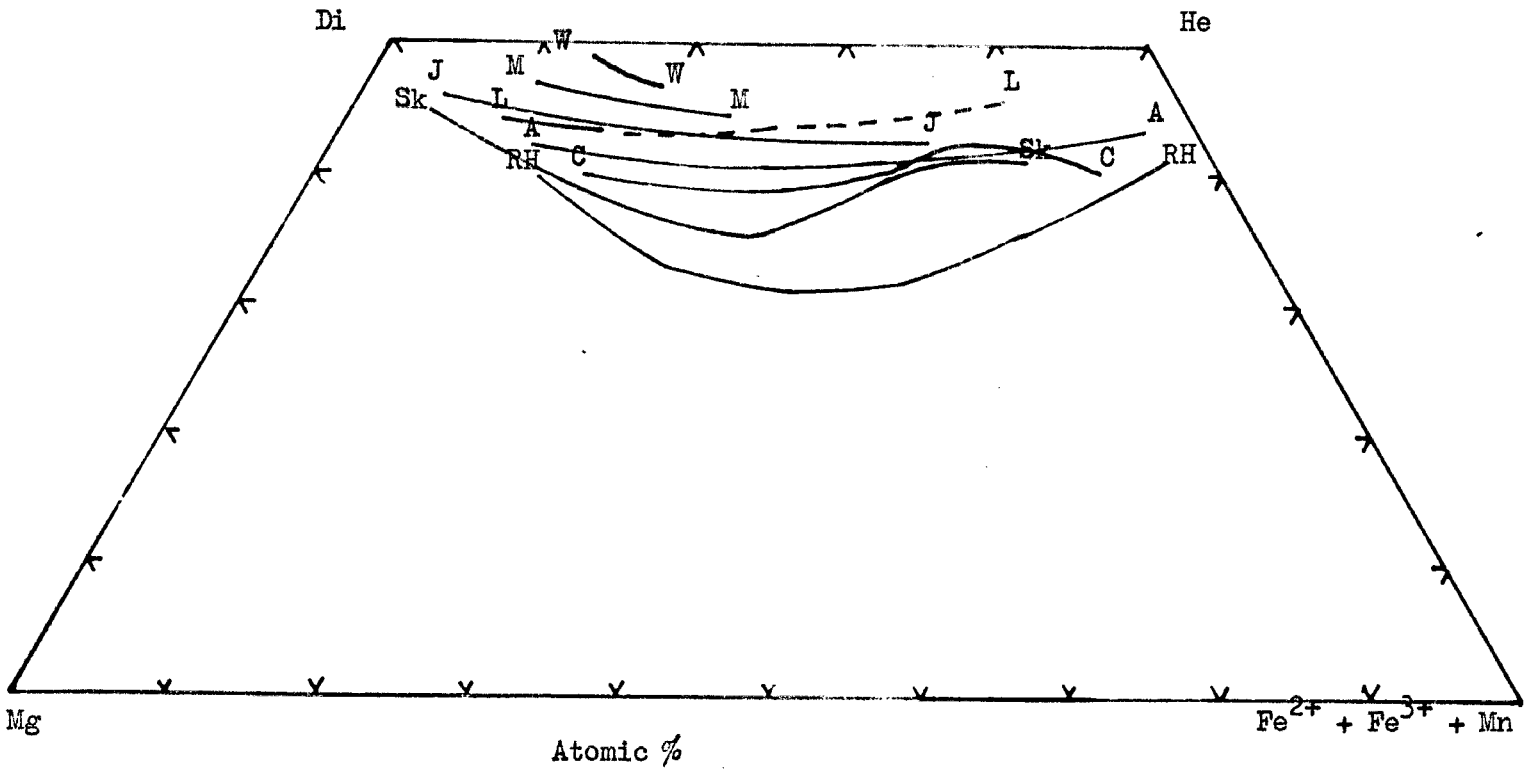

Figure 4

Plot of various clinopyroxene trends. See text for sources of data. W-W Black Jack; M-M Garbh Eilean; L-L Gough Is.; A-A Nandewars; J-J Japanese alkaline trend; C-C British and Icelandic acid pitchstones; Sk-Sk Skaergaard; RH-RH Red Hill dolerite trend.

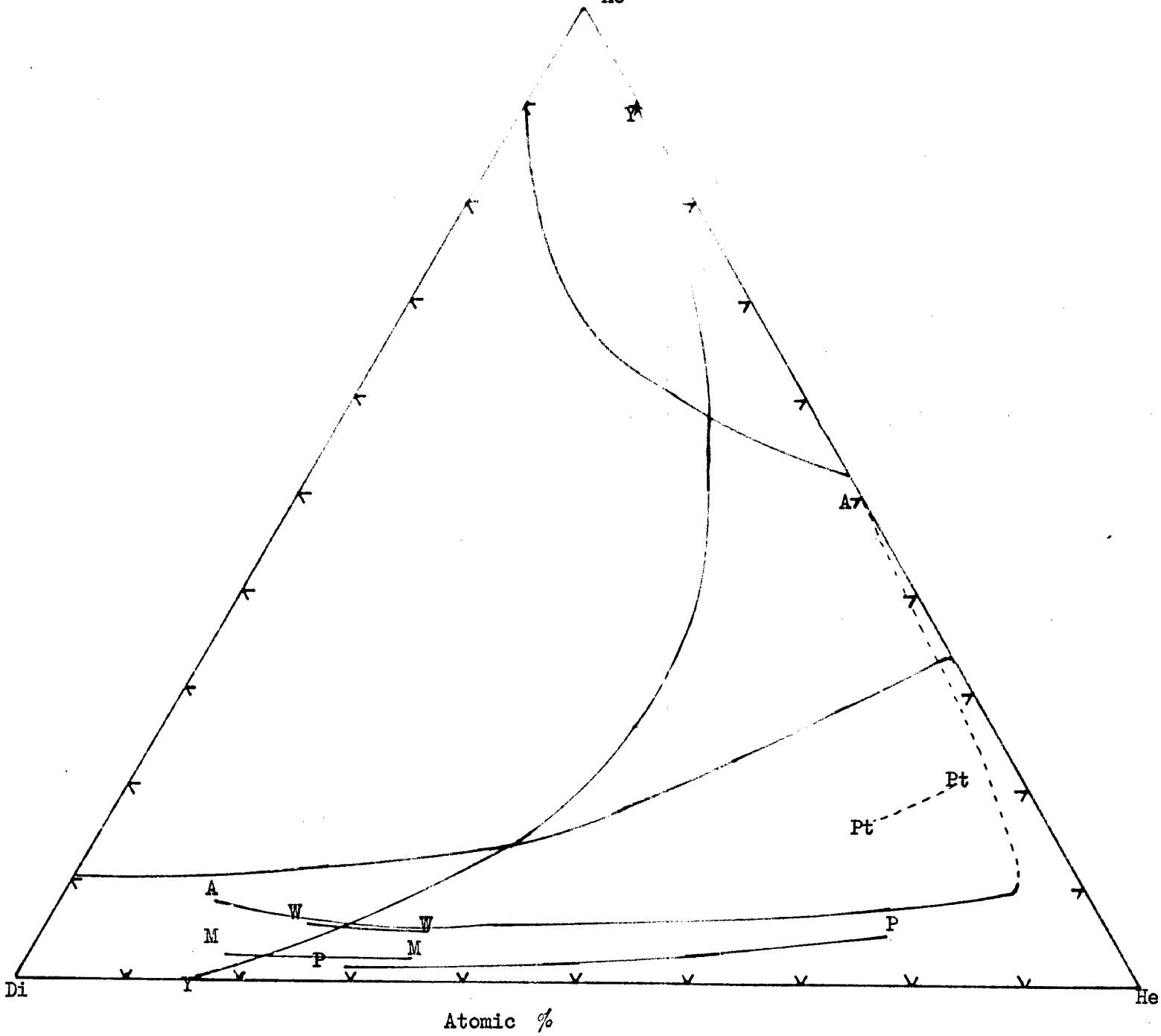

Figure 5

Plot of various clinopyroxene trends. See text for sources of data. Y-Y Morotu; P-P British and Icelandic pitchstones; Pt-Pt pantelleric sodic ferrohedenbergites; W-W Black Jack; M-M Garbh Eilean; A-A Nandewars. Aoki's suggested limits of solid solution in red.

is quite different from either the Black Jack or Garbh Eilean alkaline clinopyroxene trends; it is lower in calcium, and is also somewhat lower in calcium than the Gough Island clinopyroxenes (Fig. 4). The Black Jack and Garbh Eilean teschenites are both strongly undersaturated with respect to silica, while the Gough Island series is mildly undersaturated. The tholeiitic Skaergaard and Red Hill pyroxenes are poorer in Ca throughout than the Nandewar pyroxenes, but undergo a similar degree of Fe^{2+} enrichment. The tholeiite clinopyroxenes, however, usually show a rather pronounced fall in Ca towards the middle of the sequence when Fe^{2+} is approximately equal to Mg. The clinopyroxenes of the porphyritic acid pitchstones show similar differentiation trends to the Nandewar clinopyroxenes, but they are poorer in $NaFe^{3+}$.

Wilkinson (1956) has suggested that in the tholeiites reaction of olivine with the oversaturated magma (with respect to silica) will produce potential "hypersthene molecules". Apart from the amount of these molecules which goes to form orthopyroxene and pigeonite, a certain percentage will combine with the diopside to give an augite of lower Ca content. In undersaturated alkaline rocks, including those in which an undersaturated felspathoidal interstitial residuum prohibits a reaction of silica with olivine, the olivine, which is strongly zoned, will withdraw Mg and Mg and Fe^{2+} from the magma (and hence potential "hypersthene molecules") and the clinopyroxene crystallising will be rich in Ca. For the saturated, near saturated and oversaturated alkaline rocks, the pyroxene trend would

be expected to be intermediate between the tholeiite clinopyroxenes and the undersaturated alkaline clinopyroxenes. This study confirms that hypothesis, since all the Nandewar volcanics are saturated.

The extent of compositional changes (i.e. Fe^{2+} for Mg replacement, and $NaFe^{3+}$ for (Mg, Fe^{2+}) Ca replacement) in the clinopyroxenes has also been studied. Wilkinson (1957a) finds a very limited variation in the Fe^{2+}/Mg ratio in the clinopyroxenes despite large changes in the total rock and olivine Fe^{2+}/Mg ratios. Murray (1954) also finds that clinopyroxene variations in the teschenite at Garbh Eilean are quite restricted. However, as Le Maitre (1962) notes, differentiation in both the Black Jack and Garbh Eilean teschenites is not extreme. In the Morotu teschenite - monzonite - syenite series (Yagi, 1953) and on Gough Island (Le Maitre, op. cit.) differentiation is more complete, and the range of composition exhibited by the clinopyroxenes is greater.

The trend of clinopyroxene differentiation in the late stages depends on the oxidation state of the iron ($Fe^{3+}/Fe^{3+} + Fe^{2+}$), and also the Ca and Na contents of the magma. Aoki (1964) has discussed this question and has come to the conclusion that a diopside - hedenbergite clinopyroxene trend is due to relatively high temperatures and low partial pressures of oxygen (P_{O2}); and that this series coexists with olivine until even the later stages of differentiation; while a diopside-aegerine trend is found at lower temperatures and higher $P\ O_2$, and is associated with calciferous amphiboles in the earlier stages (hornblende, kaersutite, and hastingsite) and alkali amphiboles at later stages (riebeckite and

arfvedsonite).

The Morotu dolerite - monzonite - syenite series (Yagi, 1953) contains clinopyroxenes which grade from titanaugite, through soda-augite, aegerine-augite, to aegerine, and is an example of the clinopyroxene trend to be expected under conditions of high $P\ O_2$, which is brought about by the hydrous nature of the magma. Wilkinson (1956) has indicated that, despite the limited range of composition in the analysed clinopyroxenes from the Black Jack and Garbh Eilean teschenites, further differentiation would give a clinopyroxene richer in acmite, shown by the development of greenish rims on titanaugite crystals adjoining analcitic soda-rich mesostasis in the teschenite (Wilkinson, op. cit., p.734).

Aoki (1964) doubts whether the trend exhibited by the Morotu clinopyroxenes is an equilibrium trend, and postulates that the diopside-hedenbergite Ca-rich clinopyroxene field is separated from the acmite rich field by a wide region of immiscibility. Aoki states (op. cit., p. 1214) that the Morotu aegerine-augite (Yagi, 1953, analysis of aegerine-augite 8203, p. 782) is a mixture of soda augite cores with discrete rims of aegerine. However ".... the average clinopyroxene comppsition of the Morotu liquid changes continuously from augite to aegerine, but the clinopyroxenes crystallized from the magma are either Ca-rich or Na-rich and Ca-Na clinopyroxenes are not crystallized". (Aoki, 1964, p. 1214). Experimental evidence (Yagi, 1962, p. 98) indicates complete subsolidus solid solution between diopside and acmite, even though acmite melts incongruently to hematite + liquid. Yagi (op. cit., p. 98) is also of

the opinion that there is extensive solid solution between acmite and hedenbergite. This is supported by this study, where optical properties indicate the presence of groundmass pyroxene of the approximate composition $Ac_{50}He_{50}$.

Where the P_{O_2} of the crystallising magma is lower, the predominant trend of crystallisation of the clinopyroxene is from diopside to hedenbergite, a simple substitution of Fe^{2+} for Mg, while Ca remains constant. The Gough Island clinopyroxenes show this trend (Le Maitre, 1962), and Japanese alkaline rock clinopyroxenes, together with two sodic ferrohedenbergites from Pantelleria (Carmichael, 1962), plotted in Aoki (1964, p. 1208, Fig. 1) reveal simple diopside - hedenbergite variation. The pyroxenes from mugearites (Muir and Tilley, 1961) are also similar.

In the Gough Island rocks, the pyroxene is accompanied throughout by olivine which shows extreme enrichment in Fe^{2+}, reaching Fa_{100} in the trachytes (Le Maitre, 1962, Table 2). The co-existing clinopyroxenes and olivines in the mugearites (Muir and Tilley, 1961) show relations in the middle stages of differentiation : a more rapid increase of Fe^{2+} in the olivines than in the clinopyroxenes. The pantellerites of Pantelleria (Carmichael, 1962) and the Japanese alkaline rocks (Aoki, 1964) also have co-existing clinopyroxene and olivine throughout, and the olivines are enriched in Fe^{2+} relative to the clinopyroxenes.

In the early to middle stages of differentiation in the Nandewars in the olivine basalts and in the trachyte from Killarney Gap (KG) the clinopyroxenes are accompanied by olivine; and tie lines have been drawn

between co-existing olivines and pyroxenes (Fig. 1).

The greatest enrichment in the acmite molecule in these other series of clinopyroxenes is at Pantelleria, where one of the pantellerite clinopyroxenes has 20 per cent of the acmite component. The Nandewar analysed clinopyroxenes do not rise above 10 per cent of the acmite component (GOV4px, Fig. 2) but this analysed clinopyroxene is a phenocryst. At a later stage of differentiation, groundmass clinopyroxenes (that from trachyte 24) reveal enrichment in acmite due to greater P_{O_2} caused by the concentration of H_2O at this stage of crystallisation. The aegerine-augite from 24 is joined by arfvedsonite and cossyrite.

The Nandewar clinopyroxenes show a crystallisation trend caused by low P_{O_2} until quite a late stage, the clinopyroxene passing straight across the Di-He range of compositions, with little enrichment in Ac. Finally, with rising P_{O_2} (higher P_{H_2O}), crystallisation proceeds along the He-Ac join.

AMPHIBOLES

Amphiboles are common as late stage constituents in the trachyes, and always occur as interstitial crystals. No phenocrysts have been found.

Riebeckite - arfvedsonite

Optics:

Most of the amphiboles are alkali amphiboles of the riebeckite - arfvedsonite series. The determinable optics of this type of amphibole are:

Pleochroism and absorption:

X = dark blue-green

Y = pale violet-brown $X < Y < Z$

Z = dark green

2V = 71°, dispersion high, extinction angle small.

Miyashiro (1957) finds little difference in optical properties between riebeckite and arfvedsonite, but for the synthetic amphiboles (Ernst, 1962) which are Ca and Al free, riebeckite formed at high partial pressures of oxygen (P_{O_2}) is bright blue, and becomes greener as the solid solution becomes richer in the arfvedsonite component (formed at low P_{O_2}). The Nandewar amphiboles are quite blue.

Miyashiro (1957, p. 68) states "At least some arfvedsonites do not show complete extinction between crossed nicols even in monochromatic light". The Nandewar alkali amphiboles typically possess extreme dispersion, and complete extinction is not attained in white light, making any

precise determination of the extinction angle difficult.

X-ray data:

Ernst (1962) in a study of riebeckite and riebeckite-arfvedsonite solid solutions formed under experimental conditions, has drawn up a table (op. cit., Tables 10-11) of indexed X-ray patterns for the solid solution series. Although the present author was unable to separate pure riebeckite - arfvedsonite, a concentrate about 70 per cent pure was obtained (from analysed trachyte 24), and this was used to produce X-ray patterns with Fe $K_{\alpha 1}$ radiation (λ = 1.93597 Å). The data is compared with that of Ernst (1962) in Table 15 .

The synthetic compositions studied by Ernst (1962) range from riebeckite $oNa_2Fe_3^{++}Fe_2^{+++}Si_8O_{22}(OH)_2$ to riebeckite - arfvedsonite solid solutions of the approximate composition $(Na_{2.4}Fe^{++}_{0.6})\ Fe^{++}_{4.3}\ Fe^{+++}_{0.7}\ Si_{7.7}\ Fe^{+++}_{0.3}\ O_{22}(OH)_2$. In Table 15 , the riebeckite composition is numbered 3, and the riebeckite - arfvedsonite solid solution of the above composition is numbered 37.

From an inspection of the X-ray data in Table 15, it can be seen that the Nandewar riebeckite - arfvedsonite is closest to that of sample 37 of Ernst, a riebeckite - arfvedsonite solid solution crystallised under a partial pressure of oxygen defined by the magnetite - iron buffer. This accords well with the deduced stability relations of cossyrite (cf. section on cossyrite) where the oxidation conditions are assumed to be those defined by the magnetite - wüstite and wüstite - iron buffers. The oxidation conditions under these latter buffers are almost identical to those under the magnetite - iron buffer (Ernst, 1962, Fig. 1).

The formulae of natural alkali amphiboles (Miyashiro, 1957) are:

Riebeckite $Na_2Fe^{2+}_3Fe^{3+}_2Si_8O_{22}(OH)_2$

Arfvedsonite $Na_2Ca_{0.5}Fe^{2+}_{3.5}Fe^{3+}_{1.5}Si_{7.5}Al_{0.5}O_{22}(OH)_2$

The main substitution involved in the conversion of riebeckite to arfvedsonite is addition of Ca and Al, and conversion of some of the Fe^{3+} to Fe^{2+}.

Katophoritic Amphibole:

In two of the aegerine-augite -- cossyrite -- alkali amphibole trachytes from Castle Top Mountain (CT1 and CT2) the amphibole is of quite a distinct type, not having the typical blue colour of the riebeckite - arfvedsonite solid solutions described above, but has the following optical properties:

Pleochroism and absorption:

X = light brown-green

Y = dark brown-green $X < Y < Z$

Z = dark yellow-green

Max. extinction angle 23°, birefringence moderate.

Ernst (1962) has shown that in synthetic riebeckite - arfvedsonite solid solutions, the colour becomes greener with enrichment in arfvedsonite. Natural arfvedsonite possesses a blue-green colour in the X direction (Deer, Howie, and Zussman, 1963, vol. 2, p. 365).

The optics of the Castle Top trachyte alkali amphibole (pleochroism and extinction angle) appear to indicate a composition approaching

katophorite - $Na_2CaFe_4^{2+}Fe^{3+}Si_7AlO_{22}(OH)_2$ (Deer, Howie, and Zussman, op. cit., p. 359).

Miyashiro (1957) indicates that the series of minerals riebeckite -- arfvedsonite -- katophorite is dominated by the substitution of $CaFe^{2+}Al$ for $Fe^{3+}Si$ for Fe rich members, and in passing from riebeckite to katophorite, increasing temperatures of formation are required. A lower content of Fe^{3+} indicates a lower partial pressure of oxygen than is required for the formation of arfvedsonite.

Similar occurrences of katophoritic amphibole as dendritic, skeletal, mossy aggregates with aegerine, aegerine-augite, and aenigmatite have been noted in the trachytes of the Rungwe volcanics, Lake Nyasa (Harkin, 1960) and also in the Lake Naivasha trachte (Smith, 1931; Bowen, 1937).

TABLE 15

(d - spacings in Å)

COMPARISON OF X-RAY DATA FOR SYNTHETIC RIEBECKITE AND RIEBECKITE - ARFVEDSONITE SOLID SOLUTIONS (ERNST, 1962, TABLE 11) WITH DATA FOR THE NANDEWAR RIEBECKITE - ARFVEDSONITE FROM TRACHYTE 24.

	ERNST (1962)				Nandewar Trachyte
(hkl)	3	19	26	37	24
(110)	8.40	8.42	8.42	8.52	8.45
(200)				4.819	4.824
(040)	4.509	4.517	4.511	4.551	4.537
(131)	3.424	3.425	3.425	3.441	3.421
(240)	3.271	3.273	3.272	3.307	3.303
(310)	3.108	3.110	3.118	3.160	3.165
(330)	2.802	2.796	2.802	2.837	2.838
(151)	2.729	2.728	2.730	2.747	2.740

3 Synthetic riebeckite, partial pressure of oxygen defined by the hematite - magnetite buffer

19 Synthetic riebeckite - arfvedsonite solid solution, partial pressure of oxygen defined by the bunsenite - nickel buffer

26 Synthetic riebeckite - arfvedsonite solid solution, partial pressure of oxygen defined by the magnetite + quartz - fayalite buffer

37 Synthetic arfvedsonite - riebeckite solid solution, partial pressure of oxygen defined by the magnetite - iron buffer.

(after Ernst, 1962, Table 11).

24 Riebeckite - arfvedsonite solid solution, concentrated from trachyte 24, Nandewar Mountains.

COSSYRITE

Cossyrite is a common constituent of some of the trachytes in the Nandewar alkaline province. The term aenigmatite is synonymous with cossyrite (Shlyukova, 1963).

The cossyrite invariably occurs as an interstitial groundmass constituent, between the felspar laths of the trachytes. The analysed cossyrite trachytes (24, GOV4, Mt. W) are all peralkaline (in the sense of Shand, 1947), since they have a molecular excess of Na_2O + K_2O over Al_2O_3; and they have a moderately high TiO_2 for their stage of differentiation.

The fine grainsize of the cossyrite made separation extremely difficult. The trachyte 24, with the coarsest grainsize of the ferromagnesian minerals, was selected for the separation. The rock was crushed to pass 300 mesh sieve, and the dust washed off. The washed powder was then passed through a Franz magnetic separator to separate the ferromagnesian minerals from the quartz and felspar. Further concentration of the ferromagnesian minerals was obtained by centrifuging in methylene iodide (S.G. 3.3). The cossyrite was concentrated and partially separated from the aegerine-augite and arfvedsonite by repeated passage through a micropanner, using carbon tetrachloride as the suspending fluid. The cossyrite (S.G. 3.8) was finally purified by centrifuging in Clerici solution. The pure cossyrite concentrate was then heated over a steam bath in a dilute solution of oxalic acid (10 per cent) to remove thallium and to clean up the mineral, and remove adhering magnetite.

Optics:

The optics of the cossyrite were also difficult to determine because of the fine grainsize, strong absorption and high refractive index. Determinable properties were:

Refractive indices:

$$\left.\begin{array}{l} \alpha = 1.81 \\ \beta = 1.82 \\ \gamma = 1.90 \end{array}\right\} \pm 0.01$$

Pleochroism and absorption: X = pale yellow brown, Y = red brown, Z = dark brown, $X < Y < Z$. Extinction angle = 40°, positive elongation.

Bowen (1937) determined the optics of an aenigmatite from a pantellerite at Lake Niavasha:

Refractive indices:

$\alpha = 1.81$

$\beta = 1.82$

$\gamma = 1.88$

$2V^{+}$ small, Extinction angle = 38°.

Pleochroism and absorption: X = yellow brown, Y = brown, Z = deep brown-black, high birefringence.

Carmichael (1962) also has determined the optics of the cossyrite from the Pantelleric absidians: (Table IV)

Refractive indices:

2A	3A
$\alpha = 1.795$	$\alpha = 1.793$
$\beta = 1.805$	$\beta = 1.804$
$\gamma = 1.87$	$\gamma = 1.87$

X-ray data:

An X-ray powder photograph was taken with a Philips 114.6 cm camera with Co K radiation (λ = 1.7889 Å). The diffraction pattern is compared (in Table 16) with that of Kelsey and McKie (1964) for an aenigmatite from the Kola peninsula, and also with data for a Ti-free aenigmatite synthesized by Ernst (1962, p. 715, Table 13), and with cossyrite and aenigmatite patterns from Shlyukova (1963, p. 263, Table 2).

Shlyukova (1963) has shown that aenigmatite and cossyrite are identical, and have similar X-ray powder patterns. The cossyrite from the Nandewars is remarkably similar to the aenigmatite pattern recorded by Kelsey and McKie (1964, p. 991, Table II) from the Kola peninsula. Kelsey and McKie find that analysed cossyrites and aenigmatites from Kola, Greenland, and Pentelleria have similar X-ray patterns over the entire range of composition of the mineral. They have further tentatively indexed some of the peaks (op. cit. p. 990) from single crystal photos: 8.11 Å (001) and (010); 7.43 Å ($0\bar{1}1$); 6.38 Å ($1\bar{1}1$); the other peaks cannot be indexed.

Chemistry:

The analysis of the Nandewar cossyrite from trachyte 24 is set out beside four of the most recent analyses of the mineral (Table 17). 2A and 3A are from Carmichael (1962, Table IV), in his study of the Pantelleric obsidians; and 1 and 2 from Kelsey and McKie's analyses of aenigmatite from Khibinite quarry, Kola; and South Boswell Bay, Kangerdlugsuak, East Greenland, respectively (Kelsey and McKie, 1964, Table III).

TABLE 16

X-RAY POWDER DATA FOR COSSYRITES AND AENIGMATITES

Nandewar Cossyrite		Aenigmatite Kelsey and McKie 1964		Synth. Aenigmat. Ernst 1962		Shlyukova (1963) Table 2 Aenigmatite		Cossyrite	
d	I	d	I	d	I	d	I	d	I
8.06	10	8.11	vs	8.12	10			8.80	3
7.36	1	7.43	vw					7.97	9
6.36	2	6.38	vw						
4.82	3	4.82	w			4.709	1	4.77	1
4.41	2	4.40	w			4.112	2	4.36	1
4.18	3	4.20	w						
3.708	4	3.704	mw	3.70	3	3.657	2	3.68	3
3.463	3	3.484	w			3.428	4	3.47	3
3.155	10	3.144	vs	3.15	6	3.107	9	3.12	9
2.939	7	2.939	ms	2.95	3	2.916	9	2.93	7
2.865	1			2.94	4.5				
				2.93	5.5				
2.815	1	2.806	vw			2.785	2	2.79	2
2.756	3	2.753	vw						
2.698	9	2.705	s	2.70	5	2.680	10	2.68	8
2.657	1	2.658	vvw						
2.586	1								
2.549	9	2.545	s			2.530	10	2.53	8
2.459	2	2.462	vw						
2.418	4	2.413	m	2.41	2	2.398	3	2.40	4
2.347	1	2.347	vw			2.325	2	2.35	1
						2.300	2		
2.308	2	2.310	vw						
		2.197	vvw			2.202	1	2.19	1
2.124	8	2.119	ms	2.12	3.5	2.111	10	2.11	9
2.075	5	2.073	w			2.068	4	2.07	4
2.010	3	2.007	mw			2.003	4	2.01	6
1.977	1	1.973	vvw			1.965	1	1.946	1
1.944	5	1.947	vvw						
1.909	2	1.912	vw			1.902	3	1.910	2
1.810	1	1.808	vw			1.798	3	1.809	1
		1.772	vvw						
1.740	2	1.731	w			1.726	2	1.723	3
1.683	2	1.680	w			1.674	2	1.675	3
1.630	3	1.627	m			1.623	9	1.618	9
1.614	1	1.610	w						
1.590	1	1.59	vww			1.587	1	1.596	1
1.571	1	1.560	vww			1.557	3	1.562	1
1.517	4	1.514	w			1.513	1	1.515	4
1.500	5	1.498	mw			1.496	6	1.497	3
1.484	4	1.484	mw						
1.473	4								
1.467	4	1.468	m			1.465	10	1.467	10
1.451	6								

All d-spacings expressed in Å

TABLE 17

CHEMICAL ANALYSES OF COSSYRITES AND AENIGMATITES

	24	2A	3A	1	2
SiO_2	40.74	41.02	40.97	39.62	41.41
TiO_2	7.60	8.92	8.83	9.66	8.30
Al_2O_3	0.66	0.94	0.89	0.64	nil
Fe_2O_3	3.20	1.31	1.19	4.64	4.46
FeO	36.02	38.84	48.86	33.92	35.87
MnO	1.00	1.16	1.08	2.46	1.78
MgO	1.25	0.07	0.54	1.65	1.35
CaO	0.32	0.45	0.55	0.44	nil
Na_2O	7.29	7.36	6.93	7.20	6.87
K_2O	0.08	0.06	0.08	0.04	0.04
P_2O_5	tr				
H_2O^-	1.36		0.07	nil	n.d.
H_2O^+			nil	0.05	nil
Cl				0.02	n.d.
F				nil	n.d.
Total	99.52	100.13	99.99	100.34	100.08

24 Cossyrite from the groundmass of an aegerine-augite - arfvedsonite -cossyrite trachyte (24), Nandewar Mountains, N.S.W. Analyst M.J.A.

2A Cossyrite phenocryst from porphyritic obsidian 3112, Pantelleria.

3A Cossyrite phenocryst from porphyritic obsidian 5749, Pantelleria. 2A and 3A from Carmichael (1962, Table IV).

1 Aenigmatite from Khibinite Quarry, east of Kirovsk, Kola. Analyst J.H. Scoon.

2 Aenigmatite from South Boswell Bay, Kangerdlugsuak, East Greenland. Analyst Brown and Chadwick.
1 and 2 from Kelsey and McKie (1964, Table III).

TABLE 18

STRUCTURAL FORMULAE OF COSSYRITES AND AENIGMATITES

BASED ON 40 (O, OH), ACCORDING TO THE GENERAL FORMULA $X_4Y_{12}Z_{12}(O,OH)_{40}$

NUMBERS CORRESPOND TO THOSE OF TABLE

		24	2A	3A	1	2
[4]	Si^{4+}	11.828	11.735	11.729	11.263	11.786
	Al^{3+}	0.172	0.265	0.271	0.214	
	Fe^{3+}				0.523	0.214
	Σ4	12.000	12.000	12.000	12.000	12.000
[6]	Al^{3+}	0.054	0.052	0.029		
	Fe^{3+}	0.699	0.282	0.256	0.470	0.741
	Mg^{2+}	0.542	0.030	0.230	0.699	0.573
	Ti^{4+}	1.659	1.919	1.901	2.065	1.777
	Fe^{2+}	8.746	9.293	9.304	8.064	8.538
	Mn^{2+}	0.183	0.281	0.262	0.592	0.429
	Ca^{2+}	0.100	0.138	0.018	0.110	
	Σ6	11.983	11.995	12.000	12.000	12.058
[8]	Ca^{2+}			0.151	0.024	
	Na^{+}	4.104	4.083	3.847	3.969	3.791
	K^{+}	0.030	0.022	0.029	0.015	0.015
	Σ8	4.134	4.105	4.027	4.008	3.806
Anions						
	Cl^{-}				0.010	
	OH^{-}				0.095	
	O^{2-}	40.000	40.000	40.000	39.895	40.000
	Ox. Rat. $= \frac{Fe_2O_3 x100}{Fe_2O_3+FeO}$	8.0	2.9	2.9	11.0	10.1

The structural formulae of the analyses from Carmichael (1962) and Kelsey and McKie (1964) have been taken from Kelsey and McKie (op. cit., Table IV). The structural formula of the Nandewar cossyrite has been calculated on the basis of 40 anions per unit cell, using the formula $X_4^{[8]}\ Y_{12}^{[6]}\ Z_{12}^{[4]}\ (O,OH)_{40}$, where: X = sites of 8-fold, Y = sites of 6-fold, and Z = sites of 4-fold co-ordination, respectively. The structural formulae are set out in Table 18 .

Kelsey and McKie (1964, p. 993) state: "The assumption that Si^{4+} is confined to site of 4-fold co-ordination and that Al^{3+} and Fe^{3+} may lie on either 4-fold or on 6-fold sites require the presence of twelve and no more than twelve 4-fold sites in the unit cell. The assumption that Na^+ and K^+ lie on sites of 8-fold or higher co-ordination requires the presence of twelve 6-fold sites and four sites of high co-ordination number in the unit cell."

The calculated structural formula of the Nandewar cossyrite conforms well to this unit cell. Earlier analyses of cossyrite (Kostyleva, 1930; Gossner and Spielberger, 1929; Fleischer, 1936) are higher in Fe_2O_3 than the latest analyses and this led Fleischer to propose a unit formula $X_4Y_{13}\ (Si_2O_7)_6$ —, $Na_4Fe_9^{2+}Fe_2^{3+}Ti_2Si_{12}O_{42}$. Carmichael (1962) proposed $Na_4Fe_9^{2+}Ti_2Si_{11}O_{37}$. The idealised formula proposed on the basis of 40 oxygens by Kelsey and McKie (1964, p. 994) is $Na_4^+\ (Fe_{10}^{2+}Ti_2^{4+})Si_{12}^{4+}O_{40}^{2-}$. The Nandewar cossyrite formula is:

$$(Na,K)_{4.134}(Fe^{2+},Mn,Mg,Ca)_{9.571}(Ti,Fe^{3+},Al)_{2.402}(Si,Al)_{12.000}(O)_{40.000}.$$

The oxidation ratio ($\frac{100\ Fe^{3+}}{Fe^{2+} + Fe^{3+}}$) which is 8.0 for the

Nandewar cossyrite, lies between that of the Pantelleria cossyrites Carmichael (1962) which have an O.R. of 2.9, and thos of Kelsey and McKie (1964, Table III), with an average O.R. of 10.5.

The H_2O^- content of the Nandewar cossyrite is high (1.36 per cent), but the mineral concentrate was crushed to finer than 300 mesh during the separation procedures, and the water on the surfaces of the grains absorbed from the atmosphere would be expected to be large. The cossyrite itself is anhydrous, and appears to have no anions apart from oxygen.

The composition of the Nandewar cossyrite is not markedly different from the other analysed cossyrites and aenigmatites, showing that cossyrite crystallising at a late stage in the groundmass (Nandewars) is the same as that of earlier forming cossyrite (Kola, Pantelleria, etc.).

As shown by Kelsey and McKie (1964) the substitution of Al for Si in the 4-fold co-ordination sites is small. The total Al in the cossyrites is also small, one of the analyses quoted in Kelsey and McKie (op. cit., Table III, No. 2) having no Al at all. The earlier analyses of cossyrite tend to have higher Al, which may be due to small amounts of impurities, but it could also be due to the rhönite type substitution - CaAl for NaSi (Fleischer, 1936).

The low Al is due to peralkaline conditions under which the cossyrite is formed.

The iron is present predominantly as Fe^{2+}, indicating a low partial pressure of oxygen during crystallisation (Ernst, 1962).

Apart from Ti and Na, the amounts of any other constituents in the cossyrites is small. No study has yet been made of the trace element content of cossyrite.

Crystal structure:

Foerstner (1881) and Brogger (1890) both believed cossyrite to be a triclinic member of the amphibole series, but the X-ray studies by Gossner and Mussgung (1929) and Gossner and Spielberger (1929) showed that cossyrite could not be classified as an amphibole. Kelsey and McKie (1964) systematically studied the crystal structure of aenigmatite and suggested (op. cit. p. 996) "... that the aenigmatite unit cell contains $Si_{12}O_{36}$ in pyroxene type chains running parallel to the a-axis, the oxygen atoms of the chains being cross-linked by 6-fold co-ordinated Fe^{2+} and Ti^{4+}, which are also bonded to the four oxygen anions lying outside the chains: Na^{+} lies on sites of high co-ordination between the chains." Ti^{4+} appears to be ordered on a particular pair of 6-fold sites.

It has been suggested that the twinning seen in Pantelleric cossyrites is due to inversion of the cossyrite in cooling from a high temperature monoclinic polymorph to a triclinic polymorph (Kelsey and McKie, 1964, p. 998). The Kola and Greenland cossyrites appear untwinned, and presumably have crystallised below the inversion temperature. Similarly, the Nandewar cossyrites appear optically untwinned, and on similar reasoning, it is assumed that they have crystallised below the inversion temperature. This assumption is quite reasonable, since although both the Pantelleric and Nandewar cossyrites have crystallised from lavas, in the former case the cossyrites are phenocrysts, whereas the

Nandewar cossyrites are late stage, lower temperature minerals (the conditions of low temperature are supported by the presence of arfvedsonite).

Paragenesis:

Three conditions are essential for the formation of cossyrites:

1. Peralkalinity.
2. Low partial pressures of oxygen (P_{O_2}).
3. Concentration of TiO_2.

In the lavas of Pantelleria, where cossyrite is common (Washington, 1914, Carmichael, 1962) the pantellerites all have a molecular excess of $Na_2O + K_2O$ over Al_2O_3, resulting in the formation of acmite and the molecule sodium metasilicate (ns) in the CIPW norm. Some of the rocks even have an excess of Na_2O alone over Al_2O_3.

The Nandewar cossyrite bearing trachytes are also peralkaline, but not as markedly as the Pantelleric rocks.

Allied to the peralkalinity is a high sodium content, which in the case of the Pantelleric rocks is not reduced markedly by the formation of clinopyroxene, since this clinopyroxene has only 20 per cent of the acmite component (Carmichael, 1962, Table III). The sodium therefore becomes concentrated in the liquid with respect to Al_2O_3, CaO, and MgO, and is incorporated in cossyrite. Kelsey and McKie (1964) also note the marked enrichment of aenigmatite in Ti, Fe^{2+}, and Na and impoverishment in Al, Fe^{3+}, Mg, and Ca relative to the pyroxenes.

Ernst (1962) determined the stability limits of aenigmatite (which was titanium free) in a study of the bulk composition $Na_2O.5FeO_x.8SiO_2$

+ excess H_2O at various temperatures, total fluid pressures and partial pressures of oxygen. He found that aenigmatite existed with acmite and quartz under partial pressures of oxygen defined by the magnetite-wüstite and wüstite-iron buffers, with a pressure of water less than 1,000 bars. These partial pressures of oxygen are well below those at which magnetite exists stably (and also presumably titanomagnetite), and although the addition of titanium to the system will probably extend the field of stability of aenigmatite (Kelsey and McKie, 1964) the general nature of the stability fields are not expected to be changed.

Kelsey and McKie (1964) believe that the fact that aenigmatite has high TiO_2, and its existence as the sole titaniferous mineral of a ferromagnesian assemblage (usually including an alkali amphibole or pyroxene), shows that this mineral is an extremely favourable environment for the acceptance of Ti, and forms a titanium 'sink'. The aenigmatite will be followed in the paragenetic sequence by relatively titanium poor amphibole or pyroxene.

Carmichael (1962) tentatively suggests that the assemblage fayalite-ilmenite or fayalite - ulvöspinel could be alternative to cossyrite in Na-enriched liquids. Carmichael also adds that no sign of a reaction relationship has been found (op. cit., p. 97).

It would appear from the data of Ernst (1962) that at the relatively high partial pressures of oxygen (as defined by the fayalite $\rightleftharpoons$ magnetite + quartz buffer) the assemblage fayalite + titanomagnetite would be stable. At low partial pressures of oxygen (defined by the magnetite - wüstite,

or wüstite - iron buffers) titanomagnetite, or even ülvospinel rich magnetite, is no longer stable, and the only phase which will accept large amounts of Ti and Fe^{2+} is cossyrite.

These alternative mineral assemblages have been detected in two trachytes collected from the Governor, a coulee of trachyte in the Nandewars, on the Kaputar plateau. Both the trachytes (GOV2 and GOV4) are assumed to have similar compositions (GOV4 has been analysed). In the trachyte GOV2 the ferromagnesian assemblage is aegerine-augite + titanomagnetite, whereas in the trachyte GOV4 it is sodic ferrohedenbergite + cossyrite + arfvedsonite. From the data of Ernst (1962, Figure 11B) the assemblage magnetite + quartz + acmite can exist at a higher P_{O_2} but at the same temperature as the assemblage quartz + aenigmatite or quartz + aenigmatite + acmite at a much lower P_{O_2}. This experimental data can only be applied with great caution however: the addition of Ca and Ti to the system could affect the stability fields. Nevertheless the triple requirements of peralkalinity, low P_{O_2}, and concentration of Ti are still considered necessary for the formation of cossyrite.

TITANOMAGNETITES

Following Wilkinson (1957b) titanomagnetite has been used " ... to denote a single phase solution of TiO_2 compounds in magnetite ...." (p. 443). Buddington and Lindsley (1964) use the term 'titaniferous magnetite' to ".... designate any mineral which is predominantly magnetite and in which titanium-bearing compounds are present either in solid solution or as included phases." (op. cit., p. 311). However, Deer, Howie, and Zussman (1962, vol. 5, p. 68) believe that titanomagnetite" ...is best restricted to those specimens where the presence of an ulvöspinel phase can be demonstrated by X-ray or similar techniques ...". Titanomagnetite will be used here to denote a homogeneous single phase of magnetite with TiO_2 in solid solution.

All the alkaline rocks examined (except the leucocratic comendites) contain titanomagnetite. It is most abundant in the olivine basalts and trachyandesites, and is less abundant in the trachytes, in which it is quite sparsely distributed.

Polished sections were made of a selected example of each type of rock, and some of the titanomagnetites were separated for X-ray examination. Diffraction charts were made of each specimen, and repeated measurements of the (113) peaks of the titanomagnetites against the $(11\bar{2}0)$ of quartz were made, using Co K α_1 radiation (λ = 1.7889 Å). This enabled the cell edges a_o to be computed.

In the olivine basalt (Grl) the titanomagnetite is extremely abundant, forming numerous small euhedral crystals which are often embayed.

The titanomagnetites appear homogeneous, even under high magnification (x840) and are not noticeably pleochroic. In another olivine basalt (5P) the crystals of titanomagnetite are larger and subhedral. Some grains are anisotropic, with slight pleochroism in browns. In some crystals the anisotropic material rims anisotropic cores, whereas other crystals have channels of lighter coloured material (in reflected light).

The trachyandesites (10, 8A) have small euhedral crystals of titanomagnetite, often deeply embayed. Brown pleochroic, anisotropic crystals are common. Some titanomagnetites have pleochroic rims, others are coarsely twinned with sectors of contrasting pleochroism in browns.

The Killarney Gap trachyte (KG) has quite distinct titanomagnetites. These are large euhedral to subhedral crystals containing ilmenite exsolution lamellae oriented in two directions at 120° in the host. Some discrete blobs of ilmenite are also found at the margins of some of the larger grains. Smaller, more euhedral homogeneous crystals of titanomagnetite are also present.

The more differentiated cossyrite-riebeckite-pyroxene trachytes (24, GOV4) contain sparse large isotropic titanomagnetites, which are somewhat rounded. These titanomagnetites are nearly always rimmed with cossyrites, and in some places the cossyrite appears to be a reaction rim on the titanomagnetite.

<u>Cell dimensions</u>: The cell dimensions of the titanomagnetites are set out below:

10	trachyandesite	$a_o = 8.42$ Å	
KG	trachyte	$a_o = 8.47$ Å	↖ Ilmenite lines present
GOV4	trachyte	$a_o = 8.42$ Å	
24	trachyte	$a_o = 8.38$ Å	

The cell dimensions a_o of pure magnetite, as given by Deer, Howie, and Zussman (1962, vol. 5, pp. 72-73, Table 12) range from 8.394 Å to 8.396 Å. Lindsley (1962, p. 103, Fig. 33) plots the change in unit cell dimensions for magnetite - ulvöspinel solid solutions and shows an almost linear increase in unit cell edge from 8.397 Å for pure magnetite to 8.538 Å for pure ulvöspinel. Buddington and Lindsley (1964, p. 348, Fig. 10) have drawn a diagram showing cell dimensions of spinels in the region Fe_2TiO_4 - Fe_3O_4 - Fe_2O_3 - $FeTiO_3$. The lattice parameters have been drawn as contours in this field (after Akimoto, Katsura, and Yoshida, 1957). The cell dimensions of spinel solid solutions along the join Fe_3O_4 to $FeTiO_3$ also increase, but not in a linear manner. However, addition of either Fe_2TiO_4 or $FeTiO_3$ (in solid solution) to Fe_3O_4 will increase the cell dimensions.

Buddington and Lindsley (1964) have shown that for a titanomagnetite solid solution (Fe_3O_4 - Fe_2TiO_4), oxidation can alter the cell dimensions, and that "... there may be a wide variation in the composition and degree of oxidation of the magnetic mineral for the same value of lattice parameter." (op. cit., p. 347). They also hold that the solubility of ilmenite in magnetite is very small, and that ilmenite as exsolution lamellae and also as a component of homogeneous Fe - Ti spinels can be explained by subsolidus oxidation of Fe_2TiO_4 in magnetite - ulvöspinel

solid solutions; and further, that the oxidation of Fe_2TiO_4 occurs simultaneously with the exsolution of $FeTiO_3$.

Despite these limitations, it is possible to make some deductions regarding the composition from cell dimension data. The titanomagnetites from the trachyandesite (and presumably those from the olivine basalts) have cell edges with values quite close to that for pure magnetite, and are probably not greatly enriched in either Fe_2TiO_4 or $FeTiO_3$. The titanomagnetite from KG trachyte has a cell edge of 8.47 Å, and this, together with the presence of ilmenite exsolution lamellae in the larger crystals, indicates enrichment in $FeTiO_3$. The titanomagnetites from the trachytes GOV4 and 24 have cell edges near that of pure magnetite, and hence a great degree of enrichment in Ti is not expected, partly because the cossyrite, which often rims the titanomagnetites, absorbs the Ti from the magma.

No hematite could be detected in the polished sections studied, and this fact, together with the presence of pyroxenes rich in Fe^{2+} rather than Fe^{3+} in the early to middle stages of fractionation, and the presence of cossyrite in the trachytes, indicates a generally low to moderate P_{O_2} in the rocks crystallising titanomagnetite.

Lindsley (1963) has presented data showing that when the compositions of coexisting magnetite - ulvöspinel (Fe_3O_4 - Fe_2TiO_4) and hematite - ilmenite (Fe_2O_3 - $FeTiO_3$) solid solutions are known, in favourable cases unique solutions for the oxygen fugacity (f_{O_2}) and the temperature of their formation can be obtained. Only in the trachyte KG would it be possible to obtain this data; but because of the fine nature of the ilmenite exsolution lamellae in the magnetite, this could be difficult,

and only the temperature and oxygen fugacity at the time of exsolution would be obtained. However, some restriction can be placed on the range of partial pressure of oxygen (P_{O_2} ; related to the oxygen fugacity by the activity coefficient of oxygen). Since hematite does not appear, the fugacity of oxygen must be below that defined by the curve for the Fe_3O_4 - Fe_2O_3 transition (Lindsley, 1963, p. 61, Fig. 1). Furthermore, the temperature of crystallisation in the trachyte KG would be about 800°C. Referring to the diagram of Lindsley (op. cit., p. 63, Fig. 4), where tie lines have been drawn for coexisting Fe_3O_4-Fe_2TiO_4 and Fe_2O_3-$FeTiO_3$ solid solutions, the relations at 800°C as defined by the fayalite - magnetite - quartz buffer would approximate those present in the KG titanomagnetites - i.e. an Fe_3O_4 - Fe_2TiO_4 solid solution with about 40 per cent Fe_2TiO_4 together with an almost pure $FeTiO_3$ solid solution of $FeTiO_3$ - Fe_2O_3.

The continuance of low P_{O_2} in further differentiation of the trachytes, though not directly shown by the titanomagnetites, is shown by the reaction of magnetite to give cossyrite. Cossyrite, neglecting the Na and Si, can be regarded as $Fe_{10}Ti_2O_{14}$, or $5FeO, TiO_2$. This is a much more FeO rich composition than ulvöspinel, $2FeO.TiO_2$.

FELSPARS

The spelling of felspar used in this thesis is that recommended by Deer, Howie and Zussman (1963; vol. 4, p.4). They note that the form feldspar came from German, not from the Swedish original form. Spencer (1937) states that if any change of the name feldspar is to be made, it should be to the original Swedish feldtspar or feltspar, not to the intermediate German form feldspar. The Concise Oxford Dictionary (4th ed. 1951) notes that felspar is a false translation from the German fels: a rock. The Swedish form has priority, if any change from felspar were contemplated.

The felspars are the most abundant mineral throughout the Nandewar alkaline series and are ubiquitous. Particularly in the middle and later stages in the trachytic and comenditic rocks, the course of differentiation is controlled by the fractionation of the felspars. It is suggested that the crystallisation of large amounts of plagioclase in the 'big felspar' basalts in the early stages also has great importance on the later development of the series, and its peralkalinity.

Separation methods:

The alkali felspars were separated from several of the trachytes and comendites in order to study the trend of felspar fractionation in the middle to late stages of differentiation.

The methods of separation used closely followed those of Muir and Tilley (1961). The fine grainsize of the groundmass felspar made it imperative to use fine fractions for separation, and in general the fraction with grainsize less than 120 mesh was selected. The fine dust was washed off by decanting in water. The felspars were then separated from

the pyroxenes, amphiboles and cossyrites in methylene iodide with an S.G. of 2.7. This felspar fraction was placed in a 10 per cent solution of HCl over a steam bath for 4 hours, and extracted with a 10 per cent solution of Na_2CO_3 (Muir and Tilley, 1961). This cleaned felspar was then split into fractions of differing S.G. - in general a fraction with density less than 2.58, another with densities of from 2.58 to 2.63, and one with densities greater than 2.63. It was found in one case (KG trachyte) necessary to separate fractions with densities less than 2.55, from 2.55 to 2.58, and from 2.58 to 2.63. In most of the felspar fractions with densities greater than 2.63, quartz was present. All the other fractions consisted of anorthoclase and sanidine anorthoclase felspars.

Very small included crystals of cossyrite, clinopyroxene and amphibole were very hard to eliminate from the felspars from the trachytes GOV4 and 24, and the high content of iron (expressed as Fe_2O_3) indicates that the felspar fractions were not entirely free of these inclusions.

X-ray methods:

Each of the felspar fractions was X-rayed. Smear mounts were made of the unheated felspars, ground with quartz as an internal standard. Enough quartz was added so that the $(10\bar{1}0)$ peak was of similar intensity to the $(\bar{2}01)$ of the felspar. The samples were scanned on a Philips diffractometer from 20° to 23° and 29° to 32° several times in both directions using Cu $K_{\alpha 1}$ radiation ($\lambda = 1.541$ Å). The settings used were: diverging and scatter slits 1°, scanning speed $\frac{1}{4}^\circ$ 2θ per minute, chart speed 200 mm per hour, time constant 4, and scale factor either 4 or 8. The difference between the $(\bar{2}01)$ felspar peaks and the $(10\bar{1}0)$ of quartz were

measured, but it was found that these measurements were of little use because of the broad nature of the ($\bar{2}01$) peaks, indicating that the felspars have a broad range of composition, and possibly areas of differing thermal state. The nature of the (131) and ($1\bar{3}1$) felspar peaks were also investigated, and measurement of these peaks, together with the (220) peaks of the plagioclases, gave an indication of the thermal state.

All the felspars were then heat treated by placing in a furnace at 950°C for 24 hours, ground with quartz, and smear mounts and diffractometer charts made as before. The ($\bar{2}01$) felspar peaks sharpened noticeably after the heat treatment, and the values of Or obtained by the measurement of the average angular distance between the ($\bar{2}01$) felspar and ($10\bar{1}0$) quartz peaks (from the graph of Carmichael and Mackenzie, 1964, Figure 1) gave good agreement with the values of Or from the chemical analyses (see Tables 23-4).

The total felspar from the trachytes 100-6 and Mt W and the comenditeites Mt L and 104-E were heated and X-rayed, and the ($\bar{2}01$) peaks measured to give the bulk Or content.

The plagioclase phenocrysts from olivine basalt 5P and the total felspar from trachyandesite 10 were also X-rayed in both heated and unheated conditions. The unheated felspars were used to give patterns yielding the values of 2θ (131) - 2θ ($1\bar{3}1$) and 2θ (131) + 2θ (220) - 4θ ($1\bar{3}1$) which, if the composition of the plagioclase is known from refractive indices or other means, gives an indication of the thermal state of the plagioclase (Smith and Gay, 1958). The ($\bar{2}01$) value of the heated total felspar from trachyandesite 10 was also measured to give the Or content of this

TABLE 19

SOME OPTICAL PROPERTIES OF FELSPARS FROM ROCKS NOT ANALYSED FROM THE NANDEWARS OLIVINE BASALTS, BASALTS, AND TRACHYANDESITES.

Rock number and type		Type of felspar	R.I.	per cent An	Remarks
1	Porphyritic basalt	Plagioclase phenocrysts	β=1.567	65	Groundmass plagioclase also
CT6	Porphyritic olivine basalt	" "	β=1.565	63	" "
32	" " "	" "	β=1.565	63	" "
5	" " "	" "	β=1.563	60	" "
118-1	Porphyritic felspar basalt	" "	β=1.562	58	" "
4	" " "	" " (zoned)	α=1.564 β=1.567	66	" "
20	Trachyandesite	Rare plagioclase phenocrysts	β=1.565	63	" "
9A	" " "	" "	β=1.565	63	" "
7	" " "	" "	β=1.563 α=1.568	61	" "
2	" " "	" "	β=1.564	62	" "
20B	" " "	" "	β=1.553	40	" "
9	" " "	" "	β=1.557	47	" "

All optical determinations carried out in sodium light, accuracy of refractive indices ± 0.002.

Plagioclase compositions from the graphs of Deer, Howie, and Zussman (1963, vol. 4, pp. 130-131, Figures 48 and 49).

TABLE 20

SOME OPTICAL PROPERTIES OF FELSPARS FROM ROCKS NOT ANALYSED FROM THE NANDEWARS.

TRACHYTES.

Rock number and type		Type of felspar	Optics	Remarks
18	Porphyritic trachyte	Alkali felspar phenocrysts	β=1.533 γ=1.535	Groundmass alkali felspar also
CT2	Cossyrite-aegerine-augite-katophorite trachyte	" "	β=1.531 $2V^{-}$=70-80°	" "
Mt.F	Cossyrite-aegerine-augite-arfvedsonite trachyte	" "	β=1.529	" "
GOV1	" "	" "	β=1.534	" "
22	Two felspar trachyte	" "	β=1.535 γ=1.539 2V=62° (core) 2V=48° (margin)	Rare oligoclase phenocrysts, with groundmass alkali felspar
20A	Cossyrite-aegerine-augite-katophorite trachyte	" "	β=1.533 $2V^{-}$=70.80°	Groundmass alkali felspar in trachytic laths
26	Comendite	" "	β=1.534	Groundmass alkali felspar also

All optical determinations carried out in sodium light, accuracy of refractive indices $\pm$ 0.002.

TABLE 21

SOME OPTICAL PROPERTIES OF FELSPARS FROM ANALYSED ROCKS FROM THE NANDEWARS OLIVINE BASALTS, BASALTS, AND TRACHYANDESITES

Rock number and type		Type of felspar	Optics	Per cent An	Remarks
E7	Porphyritic basalt	Plagioclase phenocrysts	β=1.564 2V=78°	60	Groundmass plagioclase also
5P	Porphyritic olivine basalt	" "	β=1.564 (core) β=1.560 (margin) $2V^{+}$=78° (core)	63 55	" "
Gr 1	" "	" "	β=1.561 $2V^{+}$=74°	58	" "
E8	" "	" "	β=1.564 $2V^{+}$=74°	60	" "
10	Trachyandesite	Rare plagioclase phenocrysts Groundmass plagioclase	β=1.563 Ext. angle on (010)=32° α=1.556 α=1.550 Ext. angle on (010)= 28-30°	60 51 42 50-53	Total felspar has 11 per cent Or, by 201 X-ray
8A	" "	Rare plagioclase Groundmass plagioclase	α=1.559 β=1.564 α=1.547	62 36	

All optical determinations carried out in sodium light, accuracy of refractive indices ± 0.002.

Plagioclase compositions from the graphs of Deer, Howier, and Zussman (1963, vol. 4, pp. 130-131, Figures 48 and 49).

TABLE 22

E OPTICAL PROPERTIES OF FELSPARS FROM THE NANDEWARS TRACHYTES AND COMENDITES.

Rock number and type		Type of felspar	R.I. and Ext. angle	$2V_\alpha$	Remarks
118-2	Alkali syenite	Plagioclase phenocrysts	α=1.545 γ=1.555 An_{33-35}		
KG	Two felspar trachyte	Oligoclase phenocrysts	β=1.540-1.543 An_{15-20}		
		Anorthoclase phenocrysts	β=1.534-1.536 γ=1.539-1.541	56-41°	Groundmass alkali felspar also
151-2	" "	Oligoclase phenocrysts	Ext. on (010)$\bar{=}$ 11-12° An_{30}		
		Anorthoclase phenocrysts	α=1.529 β=1.536 γ=1.540	41°-55°	Cross-hatched twins
		Groundmass alkali felspar	α=1.526-1.528		Phenocrysts rimmed with alkali felspar β=1.525
24	Cossyrite-aegerine-augite-arfvedsonite trachyte	Phenocrysts alkali felspar	β=1.531-1.532	56°-61°	Groundmass alkali felspar also
GOV4	Ferrohedenbergite-arfvedsonite-cossyrite trachyte	Phenocrysts alkali felspar	α=1.526 β=1.532 γ=1.533-1.534	60-61°	" "
		Groundmass alkali fel.	α=1.526 γ=1.533		
73-5	Comendite	Alkali felspar phenocrysts	α=1.528 γ=1.535	53-59°	Groundmass alkali felspar also
73-12	" "	" "	α=1.526 γ=1.533	48°	" "
Mt W	Trachyte	" "		50-58°	Groundmass alkali felspar also; total felspar Or= 44 per cent $\bar{2}01$ X-ray
Mt L	Comendite	" "	β=1.529	42-49°	Groundmass alkali felspar also; total felspar Or= 39 per cent $\bar{2}01$ X-ray
104-E	Comendite	Alkali felspar phenocrysts	α=1.527 β=1.531-1.532 γ=1.533	52-56°	Groundmass alkali felspar also; total felspar Or= 40 per cent $\bar{2}01$ X-ray

All optical determinations carried out in sodium light, accuracy of refractice indices $\pm$ 0.002.

Plagioclase compositions from the graphs of Deer, Howie and Zussman (1963, Vol. 4, pp. 130-131, Figures 48 and 49).

plagioclase.

Occurrence and Optics of the Felspars

The optics of the felspars from the rocks not analysed are listed in Tables 19 and 20 , and those from the analysed rocks are listed in Tables 21 and 22 .

Plagioclase:

Plagioclase occurs in all the basaltic rocks: the porphyritic olivine basalts, the 'big felspar' basalts, and the trachyandesites. Oligoclase is a minor constituent of the trachytes KG and 151-2.

The 'big felspar' basalts are distinctive on account of the large felspar phenocrysts, which are extremely abundant, and up to 2 inches long. The most conspicuous feature of these phenocrysts is their zoning, which although oscillatory in type, shows progressive enrichment in Ab towards the margins. The range is from An_{65} to about An_{40}. Multiple albite and some carlsbad twinning is common. Rims of inclusions of apatites and zircons are usually developed within the crystals, just inside the margins. The cores of the phenocrysts are usually quite clear of intrusions, suggesting that these phenocrysts are of early, and perhaps intratelluric, crystallisation. In some of these basalts, the phenocryst laths of plagioclase are slightly resorbed by the magma. The groundmass plagioclases are more simply twinned and have compositions ranging from An_{50} to An_{40}. These plagioclases are usually laced with myriad apatite needles.

The plagioclases from the porphyritic olivine basalts are generally similar, but the phenocrysts are smaller and less abundant although they have the same compositional range as the phenocrysts from the 'big felspar' basalts. The groundmass plagioclases are richer in albite having a range

of composition from An_{45} to An_{25}.

The trachyandesites generally have no phenocrysts, but sometimes have up to 5 per cent of plagioclase microphenocrysts of composition of about An_{60}. These microphenocrysts are crowded with inclusions, normally show signs of severe resorption by the magma, and have some rims of potash oligoclase. The groundmass plagioclases are very fine grained, but consist generally of very small laths with trachytic flow structure, and have compositions ranging from An_{50} to An_{35}. The interstitial, low birefringence areas between the laths could be alkali felspar. A measured X-ray pattern of the total felspar fraction (heated for 24 hours at 950°C) from the trachyandesite 10 indicates an Or content of 11 per cent by the $\bar{2}01$ method (Carmichael and MacKenzie, 1964; who indicate that the ($\bar{2}01$) method gives reliable results for the Or content of ternary felspars with up to 40 per cent An). The bulk normative felspar of this trachyandesite 10 has a composition of $Or_{17}Ab_{40}An_{33}$, which indicates that the low D.R. interstitial felspar is much richer in potash than the plagioclase laths, and that it is probably calcic anorthoclase.

The bulk normative felspars of the trachyandesites 15 and 8A are much poorer in An than that of trachyandesite 10, their compositions being: 15 -- $Or_{21}Ab_{57}An_{22}$; and 8A -- $Or_{24}Ab_{64}An_{12}$. These compositions, plotted lie on the two felspar boundary of the anorthoclase field and within the anorthoclase field within the Or-Ab-An triangle, respectively (Figure 8).

Both these felspars are very fine grained with trachytic flow structure. No albite twinning of the complex or multiple type is seen, only simple carlsbad twins being present. Muir and Tilley (1961) note that in felspars of this type from mugearites, the most sodic plagioclases still

to show multiple albite twinning have a composition of Ab_{30}, and plagioclases less calcic than this show no twinning and are tentatively identified as 'lime anorthoclase'. It would appear, therefore, that lime anorthoclase forms a significant proportion of the total felspar present in these Nandewar trachyandesites (15 and 8A), the proportion being greater than for trachyandesite 10. The felspars were too fine to measure any determinative optical properties.

Oligoclase has been found in the trachytes (two felspar types) 22, 151-2, and KG. In the trachyte KG the oligoclase forms stumpy phenocrysts, which possess multiple albite twinning and are rimmed with untwinned alkali felspar. The composition (from β refractive index measurements, see Table 22) is from An_{15} to An_{20}; whereas the oligoclase phenocrysts in trachyte 151-2 have a composition of An_{30}. X-ray diffractometer measurements of the ($\bar{2}01$) peak show an average Or content in the oligoclase from trachyte KG of from 7.5 per cent to 10 per cent, from the graph of Carmichael and MacKenzie (1964, Figure 1).

The plagioclase felspars from these two felspar trachytes are similar in composition to those analysed by Muir and Tilley (1961), who note that for potash rich oligoclases, the effect of potash on the optics is a slight lowering of the refractive indices. The oligoclase phenocrysts from trachyte KG may, therefore, be slightly more An rich than An_{20}.

The thermal state of the plagioclases was investigated by X-rays.

The value for 2θ ($1\bar{3}1$) - 2θ (131) for the plagioclase phenocryst from 5P is 1.98°, which for the composition An_{63} (see Table 21) indicates an intermediate to high structural state, according to the graph of Smith and Yoder (1956). The function 2θ (131) + 2θ (220) - 4θ ($1\bar{3}1$) gives a

better indication of thermal state in the range An_{20} to An_{70} (Smith and Gay, 1958; Deer, Howie, and Zussman, 1963, vol. 4, p. 102), and the value measured on the plagioclase phenocrysts from 5P (0.93°) indicates an intermediate to high thermal state. The 2V of this plagioclase, 78°, also indicates a state approaching that of high temperature heated natural plagioclases (Smith, J.R., 1956).

The total plagioclase of the trachyandesite 10 has an assumed composition, ignoring Or content, of An_{40-45} (from an average of the optical values An_{50}, and bulk normative felspar An_{38-40}). The value of $2\theta\ (1\bar{3}1) - 2\theta\ (131)$ for this felspar is 1.78°, which indicates a low temperature plagioclase according to the graph of Smith and Yoder (1956) and the value $2\theta\ (131) + 2\theta\ (220) - 4\theta\ (1\bar{3}1)$ of 0.50° indicates a state approaching low temperature plagioclase (Smith and Gay, 1958). The values of $2\theta\ (1\bar{3}1) - 2\theta\ (131)$ and $2\theta\ (131) + 2\theta\ (220) - 4\theta\ (1\bar{3}1)$ especially for low temperature plagioclases, are essentially constant in the range An_{40-45} (Smith and Yoder, 1956; Smith and Gay, 1958).

Comparing the 2V of plagioclase phenocrysts from basalts E7, Gr 1, and E8 with the composition derived from β refractive indices on the graph of Smith J.R. (1956) yields data on the thermal state, and this is set out below:

Rock	Refractive index	Per Cent An	$2V^{\circ}$	Indicated thermal state
E7	β=1.564	60	78	Intermediate
Gr 1	β=1.561	58	74	High
E8	β=1.564	60	74	High

The plagioclase phenocrysts from the basalts are generally in an

intermediate to high thermal state, while the total plagioclase from the trachyandesite 10 has a thermal state approaching low temperature forms.

Alkali felspar:

In the zoned felspars of the trachyandesites it appears that the low D.R. interstitial areas of felspar between the laths of carlsbad and albite twinned oligoclase are calcic anorthoclases, similar to the types described by Muir and Tilley (1961) from mugearites. The bulk normative felspar of these trachyandesites (10, 15, 8A), when plotted on an An-Ab-Or diagram (Fig. 8), lie near, or within the anorthoclase field, as defined by Smith and MacKenzie (1958), and hence much of the felspar must be anorthoclase.

The two felspar trachytes contain both phenocryst and groundmass anorthoclase. The phenocrysts are stumpy, unlike the elongated lath-shaped felspars present in other trachytes. The (001) and (110) forms, and a rhomboidal outline are developed, rather than elongation parallel to (010). Upton (1964) has observed this rhomboidal shape in alkali felspars in alkali rocks in South Greenland, and concludes that in these cases the felspars crystallised as relatively Ca-rich monoclinic soda-sanidines, and subsequently inverted to triclinic symmetry. Oftedahl (1948) in studying the rhomb porphyries of the Oslo region, considers that the rhomboidal felspars crystallised as plagioclases; but Upton (op. cit.) notes that plagioclase, crystallised initially as the triclinic form (because the liquidus is below the temperature of the monoclinic - triclinic inversion; Smith and MacKenzie, 1958) has tabular habit, but once the felspar begins to crystallise initially as the monoclinic form (calcic anorthoclase), rhomboidal habit is assumed.

In the trachyte from Killarney Gap (KG), the anorthoclase phenocrysts have usually developed blotchy or patchwork extinction, together with faint traces of cross-hatched twinning in many cases. The blotchy extinction is taken to indicate one of three phenomena:

1. Differing thermal states.
2. Differing compositions (only a slight difference assumed).
3. Exsolution.

The last possibility is favoured, as the blotchy extinction appears like that in mesoperthites, and in the Nandewar anorthoclases there could be exsolution of an Ab rich phase from an Or rich phase. This exsolution appears to have taken place before extrusion, since the phenocrysts are rimmed with homogeneous alkali felspar with a lower R.I.

The anorthoclase phenocrysts from trachyte KG contain up to 8 per cent An (from chemical analysis of felspar fractions), and the refractive index, $\beta = 1.535$). Oftedahl (1948) has produced curves from the average refractive index $\frac{1}{2}(\alpha + \gamma)$ and the extinction angle α a, for the composition of ternary alkali felspars with up to approximately 10 per cent An. Knowing the composition of the felspars from the chemical analyses (Table 23), the average refractive index for these anorthoclases N = 1.534, is higher than predicted from the graph of Oftedahl, and this highlights the difficulty of producing optical determination curves for the ternary felspars. The β index is also higher than predicted from the graph of Tuttle (1952) where β refractive indices along the (An + Ab) - Or join are plotted. The An molecule in the anorthoclases will raise the refractive indices, and Deer, Howie and Zussman (1963, vol. 4) note that the effects of quite small amounts of An in solid solution will have relatively large effects on the

refractive indices, as also will small amounts of Ba, Sr, Rb and Fe^{3+}.

MacKenzie and Smith (1956) consider that refractive indices change but slightly with composition in the high temperature alkali felspar series in the Ab - Or system, and that the values for the different structural states (high and low temperature forms) vary only slightly. They conclude, that for R.I. measurements to be of any value, they must be determined much more accurately than has been done in the past. It is also clear from the graph of Tuttle (1952, Fig. 2) that the variation in R.I. for high temperature alkali felspars between pure Or and pure Ab is quite small (γ = 1.522 to 1.534, α = 1.518 to 1.526). These changes, as noted before, could be overshadowed by small amounts of Ca.

Since there are so many factors which can influence the refractive indices of the alkali felspars, particularly the ternary felspars, the use of R.I. in determining compositional changes is of very doubtful value, except perhaps for giving some estimate of the extent of Ca in solid solution in the felspars. The use of optic axial angles, together with the known chemical composition, or the Or/Ab ratio from X-ray $\bar{2}01$ determinations, gives much more valuable information, particularly on the structural state of the felspars, and this aspect will be discussed later.

The groundmass felspars of the two felspar trachytes are much more elongated parallel to (010) and lath-shaped, and possess carlsbad twinning.

The anorthoclase phenocrysts in trachyte 22 are generally similar to those in the Killarney Gap trachyte KG, but show much better developed cross-hatched twinning, and much less exsolution. This indicates that trachyte 22 has cooled through the inversion temperature, but has not cooled slowly enough for exsolution to develop. Smith and MacKenzie (1958) state

that the sanidine - anorthoclase inversion is almost instantaneous, so that even with very fast cooling, the cross hatched twinning should develop. Another reason for the lack of exsolution is that, for the composition of the anorthoclase under consideration (soda-rich), the alkali felspar solvus lies at about 400°C. When the rock has cooled to this extent, the sluggishness of solid state diffusion will probably prevent exsolution from taking place (Smith and MacKenzie, op. cit.).

The anorthoclase phenocrysts from trachyte 151-2 are less rhomboidal than those just described from trachyte 22. They are more elongated and lath-shaped, and have quite common carlsbad twinning, and less common tartan twinning. A tendency for the anorthoclase phenocrysts to form glomeroporphyritic aggregates was noted. The groundmass felspars from this trachyte (151-2) are small elongated laths in trachytic flow structure, and usually possess carlsbad twins. The R.I. of this groundmass felspar is lower than that of the phenocrysts (phenocrysts $\alpha = 1.529$; groundmass $\alpha = 1.526$).

The anorthoclases from the mugearites studied by Muir and Tilley (1961) have from 10 per cent to 20 per cent An. Those with 10 per cent An have average refractive indices $\alpha = 1.526$, $\gamma = 1.535$, and those with from 11 per cent to 13 per cent An have average refractive indices $\alpha = 1.526$-1.531, $\gamma = 1.536$-1.540. The anorthoclase phenocrysts from the two felspar trachytes in the Nandewars have average refractive indices of $\alpha = 1.529$, $\beta = 1.535$, $\gamma = 1.540$, and these values are close to those of the anorthoclases from the mugearites with 11 per cent to 12 per cent An (Muir and Tilley, 1961).

The alkali felspars from the one felspar trachytes and comendites are members of the sanidine - anorthoclase series (Tuttle, 1952), with much lower An than the anorthoclases from the two felspar trachytes.

Most of the one felspar trachytes and comendites are porphyritic, with phenocryst laths of felspar set in a groundmass of smaller felspar laths with trachytic flow structure. There are few exceptions; comendite 73-5 is fine grained throughout, and comendite 73-12 has an orthophyric texture, being made up of stumpy laths of felspar with a finer interstitial quartz - felspar matrix. These laths all show signs of strain and possess undulose extinction, and have many cracks across the laths, indicating the intrusion of this comendite as a crystal 'mush'.

Upton (1964) has noted that the rhomboidal felspars (present in some volcanic provinces as rhomb-porphyries, and in the Nandewar province in some of the two felspar trachytes) with $(1\bar{1}0)$, (110),(210) forms become progressively modified in differentiating magmas with the appearance of (010) faces, although in the acid series in the Tugtutoq rocks in East Greenland, the (001) form achieves equal prominence, leading to rectangular rather than tabular crystals (Upton, 1964).

In the Nandewar one felspar trachytes and comendites the development of tabular form parallel to (010) in the felspars predominates, but in some phenocrysts the development of the (001) form does give the crystals a rectangular aspect.

MacKenzie (1952) and Smith and MacKenzie (1958) have studied the temperature of the monoclinic - triclinic inversion in the soda-rich felspars. For the sanidine-anorthoclase felspars at present under consideration, with an approximate composition (subracting An) of from $Ab_{65}Or_{35}$ to $Ab_{60}Or_{40}$ (Table 24), the monoclinic - triclinic inversion temperature is 200°C or less. Compositions from approximately $Ab_{63}Or_{37}$ to Or_{100} are monoclinic (Smith and MacKenzie, 1958), and the range of composition of the felspars from the Nandewar one felspar trachytes and the comendites indicates

that they would be either monoclinic or very close to monoclinic. There is thus no monoclinic - triclinic inversion for the monoclinic felspars, and for the felspars which closely approach monoclinic symmetry, the inversion produces little change in cell dimensions, so no cross-hatched twinning is produced. The monoclinic crystals are intially precipitated as monoclinic soda-sanidines, and remain so on cooling.

The sanidine-anorthoclase felspars from the one felspar trachytes and comendites generally possess only carlsbad twinning in both phenocrysts and groundmass crystals. In some of the phenocrysts the composition plane of the carlsbad twins tends to be rather irregular, and some baveno twinning has been detected, especially in those felspars possessing rectangular outlines bounded by (001) and (010) faces.

Some of the felspar phenocrysts have slightly blotchy extinction, indicating exsolution of Ab rich phases from Or rich phases. The solvus for the composition of these felspars ($Ab_{65}Or_{35}$) lies in the range 550° to 650°C (Smith and MacKenzie, 1958). The absence of marked exsolution is no doubt due to the extreme rapidity of cooling of these magmas, and perhaps also to relatively anhydrous environments.

The refractive indices of these felspars are somewhat lower than those for the anorthoclases from the two felspar trachytes (Tables 20 and 22). The average refractive indices are: α = 1.526-1.527, β = 1.530-1.533, γ = 1.533-1.535 (compared to the average refractive indices from the anorthoclases in the two felspar trachytes, α = 1.529, β = 1.535, γ = 1.540). The smaller content of An in the sanidine - anorthoclases produces the lower refractive indices.

Structural and Thermal state:

It was stated earlier that if the composition of an alkali felspar was known, the structural and thermal state could be deduced from the graph of Tuttle (1952, Fig. 1).

The 2V of selected felspars has been measured with a Leitz 4 axis universal stage, using sodium light, by orthoscopic and conoscopic methods. In general, only the 2V values for the phenocrysts could be measured. The composition of these phenocrysts has been taken as the most calcic of the chemically analysed felspar fractions (reduced to Ab-Or, by subtracting An) where an analysis is available, or from measurements. Several values of 2V were measured on the phenocrysts from each rock, and a maximum variation within the one crystal of 14° in 2V has been found.

Le Maitre (1962) has noted a similar feature from the felspars in the Gough Island rocks, and Tuttle and Keith (1954) in a study of felspars from the Beinn an Dubhaich granite find variation from 10° to 15° in 2V quite common in felspars from one rock. Tuttle and Keith assume that the variation is due to transitional structural states, the composition of the felspar within any one rock being constant. Le Maitre (1962) assumes that a similar situation exists in the felspars from Gough Island, but is doubtful whether all variation in 2V is due to transitional structural states, and some of the variation is ascribed to compositional differences. It should be noted that the curve of Tuttle (1952, Fig. 1) showing the variation in 2V of the sanidine-anorthoclase series is reasonably flat (constant) in the region of composition of the Nandewar alkali felspars (at from approximately $Ab_{70}Or_{30}$ to $Ab_{60}Or_{40}$); and that for a 10 per cent variation in Or content (from Or_{30} to Or_{40}), the 2V of the felspar series changes by only $3\text{-}4^{\circ}$.

Therefore most, if not all, of the variation in 2V in the Nandewar volcanic felspars is due to differences in structural state. All the 2V measurements indicate that the optic axial plane is approximately perpendicular to (010); thus the felspars are close to the sanidine-anorthoclase series of Tuttle (1952).

The values of 2V are plotted against the composition in terms of Ab and Or in Fig. 6 , which is drawn after Tuttle (1952, Fig. 1). The different alkali felspar series of Tuttle have been inserted in the diagram, and all the Nandewar felspars studied possess transitional structural states between the sanidine-anorthoclase and low albite-orthoclase series, but are much closer to the sanidine-anorthoclase series, being just on the low temperature side of that series. The relatively small range of composition of the felspars is to be expected, since they approach the minimum melting composition $Ab_{65}Or_{35}$.

In an anorthoclase phenocryst from a two felspar trachyte (22), the 2V varies from 62° at the core, to 48° at the margin. Part of this variation is due to compositional differences in zoning of the felspar (but as mentioned before, this could only account for a small part of the 2V variation), and the main variation is due to differences in structural state. It is interesting to note, therefore, that the core has optics indicating that it is closer to the low temperature low albite-orthoclase series than the margin, which is close to the sanidine-anorthoclase series in structural state. It would appear that the phenocryst began crystallisation in an intratelluric environment, and had partly inverted to a low temperature state before extrusion. Upon extrusion, the temperature was sufficiently high to cause felspars to crystallise in higher temperature forms. It is also significant that any exsolution seen in the felspar phenocrysts is restricted to the

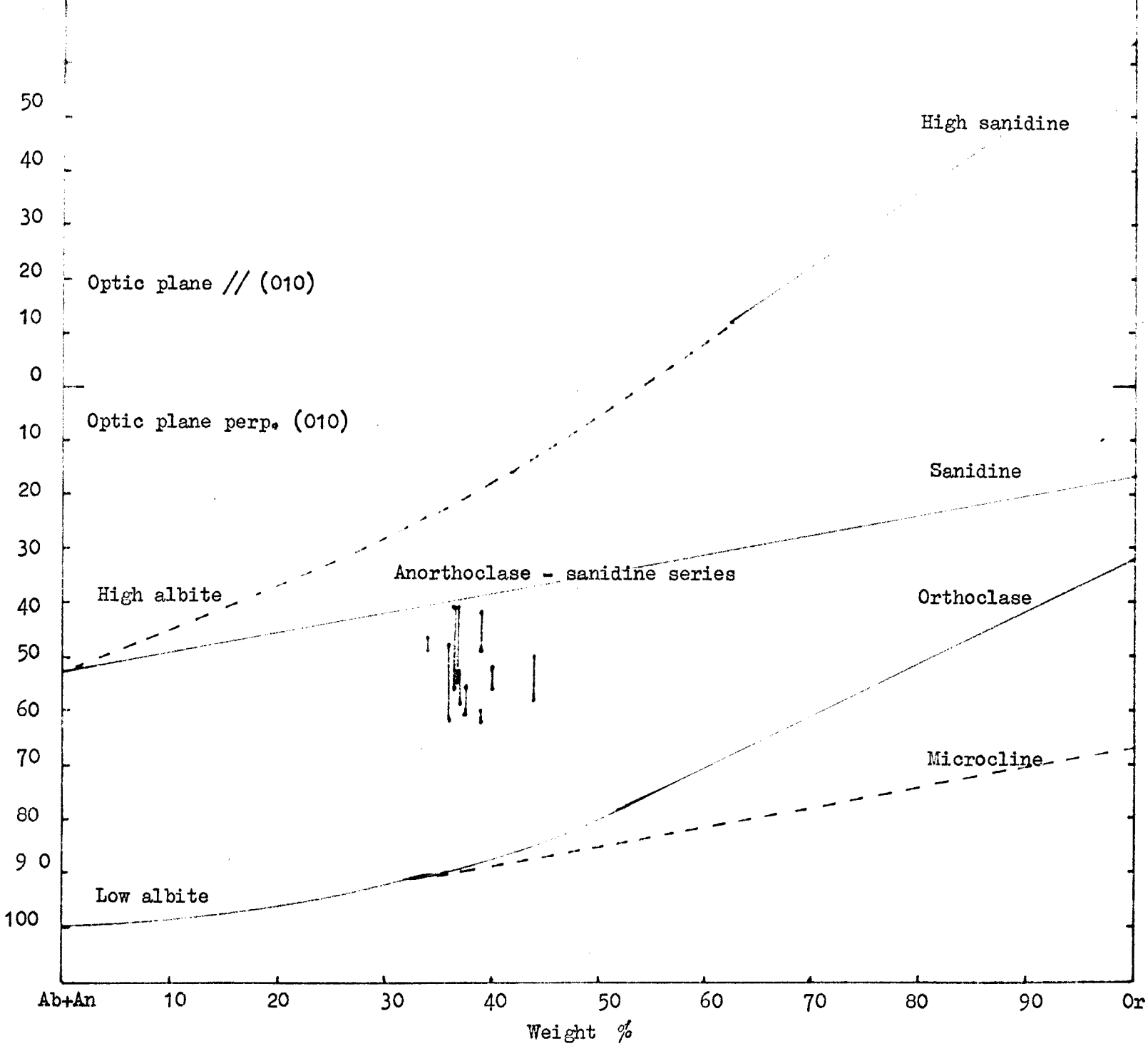

Figure 6

Relation between optic axial angles and structural states and composition of alkali felspars. Graph after Tuttle and Bowen (1958) and Tuttle (1952).

cores of the crystals, while the margins consist of quite homogeneous alkali felspar.

Chemical analyses of alkali felspars:

Several felspar fractions were separated (see above) from each of the following rocks:

KG two felspar trachyte

24, GOV4 one felspar pyroxene - amphibole - cossyrite trachytes

73-5, 73-12 comendites

The specimen numbers, rock types and localities are set out in Table 28. The analyses (for SiO_2, Al_2O_3, Fe_2O_3, CaO, Na_2O and K_2O) are set out in Tables 23 and 24. The 'total felspar component' indicates that Fe_2O_3 has been subtracted from the total (all the iron is stated as Fe_2O_3, as FeO has not been determined). The percentages by weight of Q, or, ab, an; and or, ab, an respectively are also set out in Tables 23 and 24, together with per cent or determined by the X-ray $\bar{2}01$ method.

It has previously been noted that the felspar fraction with S.G. greater than 2.63 from various rocks contains quartz (see Tables 23 and 24, where 73-5 AF 3 and 73-12 AF 3 contain 80.43 per cent and 88.04 per cent SiO_2, respectively). It can further be seen that all the felspar fractions contain quartz in varying amounts.

The procedure adopted in calculating the felspars was as follows: to the molecular amounts of Ca, Na, and K, an equal molecular amount of Al_2O_3 is added, plus twice the molecular amount of SiO_2 (to the Ca for An) or six times the molecular amount of SiO_2 (to Na and K for Ab and Or). Any excess SiO_2 was calculated as quartz. No attempt has been made to calculate structural formulae, because of the excess quartz and the presence of other

TABLE 23

CHEMICAL COMPOSITION OF FELSPAR FRACTIONS FROM ANALYSED TRACHYTES IN THE NANDEWARS.

ANALYST M.J. ABBOTT.

	KG			73-5		
	AF 1	AF 2	AF 3	AF 1	AF 2	AF 3
SiO_2	68.32	67.04	66.44	65.75	66.59	80.43
Al_2O_3	17.21	18.16	18.71	19.65	19.22	11.28
Fe_2O_3	0.45	0.43	0.48	0.53	0.45	0.28
CaO	0.65	0.82	1.59	0.44	0.66	0.47
Na_2O	5.88	6.58	6.88	6.16	6.95	4.03
K_2O	6.55	6.74	5.69	6.67	6.46	3.51
Total	99.06	99.77	99.79	99.20	100.33	100.00
Total felspar component	98.61	99.34	99.31	98.67	99.88	99.72
Q	7.66	1.21	1.56	3.43		42.56
or	38.71	39.83	33.63	39.45	38.18	20.74
ab	49.76	55.68	57.75	52.13	58.84	34.09
an	3.23	4.07	7.89	2.18	3.27	2.33
or	42.2	40.0	33.9	42.1	38.1	36.3
ab	54.3	55.9	58.2	55.6	58.7	59.6
an	3.5	4.1	7.9	2.3	3.2	4.1
or (X-ray)	43.0	37.5	35.0		37.2	38.0

From rock KG

KG AF 1: Alkali felspar fraction with S.G. less than 2.55.
KG AF 2: Alkali felspar fraction with S.G. between 2.55 and 2.58.
KG AF 3: Alkali felspar fraction with S.G. between 2.58 and 2.63.

From rock 73-5

73-5 AF 1: Alkali felspar fraction with S.G. less than 2.58.
73-5 AF 2: Alkali felspar fraction with S.G. between 2.58 and 2.63.
73-5 AF 3: Alkali felspar fraction with S.G. between 2.63 and 2.65.

TABLE 24

CHEMICAL COMPOSITION OF FELSPAR FRACTIONS FROM ANALYSED TRACHYTES IN THE NANDEWARS.

ANALYST M.J. ABBOTT.

	73-12			24		GOV4	
	AF 1	AF 2	AF 3	AF 1	AF 2	AF 1	AF 2
SiO_2	70.40	68.16	88.04	67.28	67.59	69.07	71.04
Al_2O_3	16.83	18.47	6.89	18.33	18.96	16.22	15.84
Fe_2O_3	0.79	0.63	0.33	0.94	0.94	1.15	1.26
CaO	0.06	0.12	0.03	0.16	0.23	0.11	0.18
Na_2O	7.77	7.71	2.97	6.53	7.07	6.38	5.90
K_2O	5.13	5.48	2.05	6.40	6.16	6.03	5.70
Total	100.98	100.57	100.31	99.64	100.95	98.96	99.92
Total felspar component	100.19	99.94	99.98	98.70	100.01	97.81	98.66
Q	10.89	2.85	63.33	4.34	2.40	8.64	14.52
or	30.32	32.39	12.12	37.82	36.40	35.64	33.69
ab	58.01	64.50	24.44	55.26	59.83	53.99	49.93
an	0.30	0.60	0.15	0.79	1.14	0.55	0.89
or	34.2	33.2	33.0	40.3	37.4	39.5	39.9
ab	65.5	66.2	66.6	58.9	61.4	59.9	59.1
an	0.3	0.6	0.4	0.8	1.2	0.6	1.0
or (X-ray)		34.5	32.5	38.1	38.0	39.0	39.5

From rock 73-12

73-12 AF 1: Alkali felspar fraction with S.G. less than 2.58.
73-12 AF 2: Alkali felspar fraction with S.G. between 2.58 and 2.63.
73-12 AF 3: Alkali felspar fraction with S.G. greater than 2.63.

From rock 24

24 AF 1: Alkali felspar fraction with S.G. less than 2.58.
24 AF 2: Alkali felspar fraction with S.G. between 2.58 and 2.63.

From rock GOV4

GOV4 AF 1: Alkali felspar fraction with S.G. less than 2.58.
GOV4 AF 2: Alkali felspar fraction with S.G. between 2.58 and 2.63.

impurities. Some calculations were made, however, to gauge the extent to which Fe_2O_3 entered the felspar formula. It was found that for 24 AF 1 and 24 AF 2 no Fe^{3+} enters the felspar, and there is a molecular excess of Al of 0.004 and 0.002, respectively; for GOV4 AF 1 and GOV4 AF 2 balance to the formula was achieved by adding all the Fe^{3+} to the Al; for KG AF 1, KG AF 2, and KG AF 3 there was charge balance, 0.01 and 0.011 molecular excess of alkalies, respectively; and for 73-12 AF 1, 73-12 AF 2, and 73-12 AF 3 there is a molecular excess of 0.011 alkalies and charge balance for the other two fractions, respectively; and for 73-5 AF 1, 73-5 AF 2, and 73-5 AF 3 there is a molecular excess of Al of 0.014, 0.006, and charge balance, respectively. All the molecular units are expressed relative to 16.000 oxygens according to the formulae $(K,Na)_2(Al,Si_3)_2O_{16}$ and $Ca_2(Al_2Si_2)_2O_{16}$.

Deer, Howie and Zussman (1963, vol. 4, Table 7) record departures of up to 0.06 formula units from the ideal $(Al,Si)_8$ and up to 0.07 formula units form the ideal $(K,Na)_2$ in anorthoclases analysed by various workers. The departures from the ideal formulae for the Nandewar alkali felspars are all thus well within these limits.

Since the felspar fractions analysed are not pure, no comment can be made on the suggestion of Chayes and Zies (1962) that there is a possibility of a systematic departure from the assumed ratio 1:1:6 in $RO:R_2O_3:SiO_2$ in alkali felspars, and like Carmichael and MacKenzie (1964) the present author will assume that the 1:1:6 ratio is adhered to.

The question of whether Fe^{3+} enters the felspar structure cannot definitel be decided from the data for the Nandewar alkali felspars. Chayes and Zies (1962) attribute the buff colour obtained by heating the felspars in air at about 850°C to the presence of Fe^{3+} proxying for Al in the structure. Many

of the Nandewar alkali felspar fractions, when heated in air at about 950°C for X-ray study, took on a buff tint. It is therefore assumed that Fe^{3+} does enter the Nandewar alkali felspars. Deer, Howie and Zussman (1963, vol. 4) find that Fe^{3+} in anorthoclases can reach up to 0.40 per cent (as Fe_2O_3) even in glass clear crystals, and that it replaces Al.

The or, ab, and an percentages by weight were calculated by subtracting Q and recalculating to 100 per cent : these values have been plotted in Fig. 7 .

The X-ray values for the weight per cent or agree quite well with the chemical values (Tables 23 and 24), and no systematic error between the two sets of determinations has been found, contrary to the results of Chayes and Zies (1962). The small amount of An in each felspar does not affect the X-ray $\bar{2}01$ determinations (Carmichael and MacKenzie, 1964).

Apart from the Na, which was determined by flame photometer, all the oxides have been determined by X-ray fluorescence, and in some cases the totals are outside the 100.5 - 99.5 per cent limit. The variation in the totals is from 99.0 - 101.0 per cent. Carmichael and MacKenzie (1964) believe that for pure felspars, it is only necessary to determine CaO, Na_2O, and K_2O (also BaO and SrO where present in significant amounts); and further that the recalculated felspar composition then should be in the range of from 98.0 to 102.0 per cent in a reasonably good analysis. The present author believes it is wise to determine the SiO_2 and Al_2O_3 as well, particularly when even apparently pure samples of felspar have excess SiO_2 (Chayes and Zies, 1962), existing within the felspar as microscopic and sub-microscopic films and blebs of quartz.

Trends of felspar crystallisation:

The theoretical aspects of felspar crystallisation in the ternary

system $CaAl_2Si_2O_8$ - $NaAlSi_3O_8$ - $KAlSi_3O_8$ have been considered in recent publications: Tuttle and Bowen, 1958; Turner and Verhoogen, 1960; Stewart and Roseboom, 1962; and Carmichael, 1963; and the crystallisation in the quaternary system $CaAl_2Si_2O_8$ - $NaAlSi_3O_8$ - $KAlSi_3O_8$ - SiO_2 has also been considered by Carmichael, 1963.

Data for crystallisationof felspars in natural rocks has been presented by many workers, and some of the recent work has been that of Oftedahl (1948), Carmichael (1960b, 1963), Muir and Tilley (1961), Le Maitre (1962), and Upton (1964).

The relationships in the system $CaAl_2Si_2O_8$ - $NaAlSi_3O_8$ - $KAlSi_3O_8$ have been projected onto the An-Ab-Or plane (Fig. 7). Solid solution in this ternary system is essentially limited to the binary pairs An-Ab and Ab-Or, and the extent of ternary solid solution between An, Ab, and Or is temperature dependent. Tuttle and Bowen (op. cit., p. 132, Fig. 64) show a greater amount of ternary solid solution than Turner and Verhoogen (1960, p. 112, Fig. 11). Carmichael (1960b) also shows a rather more restricted field of ternary solid solution than Tuttle and Bowen. The discrepancy between the fields of solid solution as shown by Tuttle and Bowen (1958) and Turner and Verhoogen (1960) can be resolved, according to Turner and Verhoogen (op. cit., p. 116) " .... if allowance is made for the appearance of such minerals is biotite, hornblende, sphene, fluorite, and carbonates in the modes of the rocks concerned."

If the normative composition of the magma (in terms of An, Ab, and Or) lies in the field extending from the An-Or join towards the Ab apex, then two felspars, an An + Ab rich and an Or rich, will crystallise, and this field is thus known as the two felspar field. This two felspar field is caused by the intersection of the solvus with the solidus in the ternary

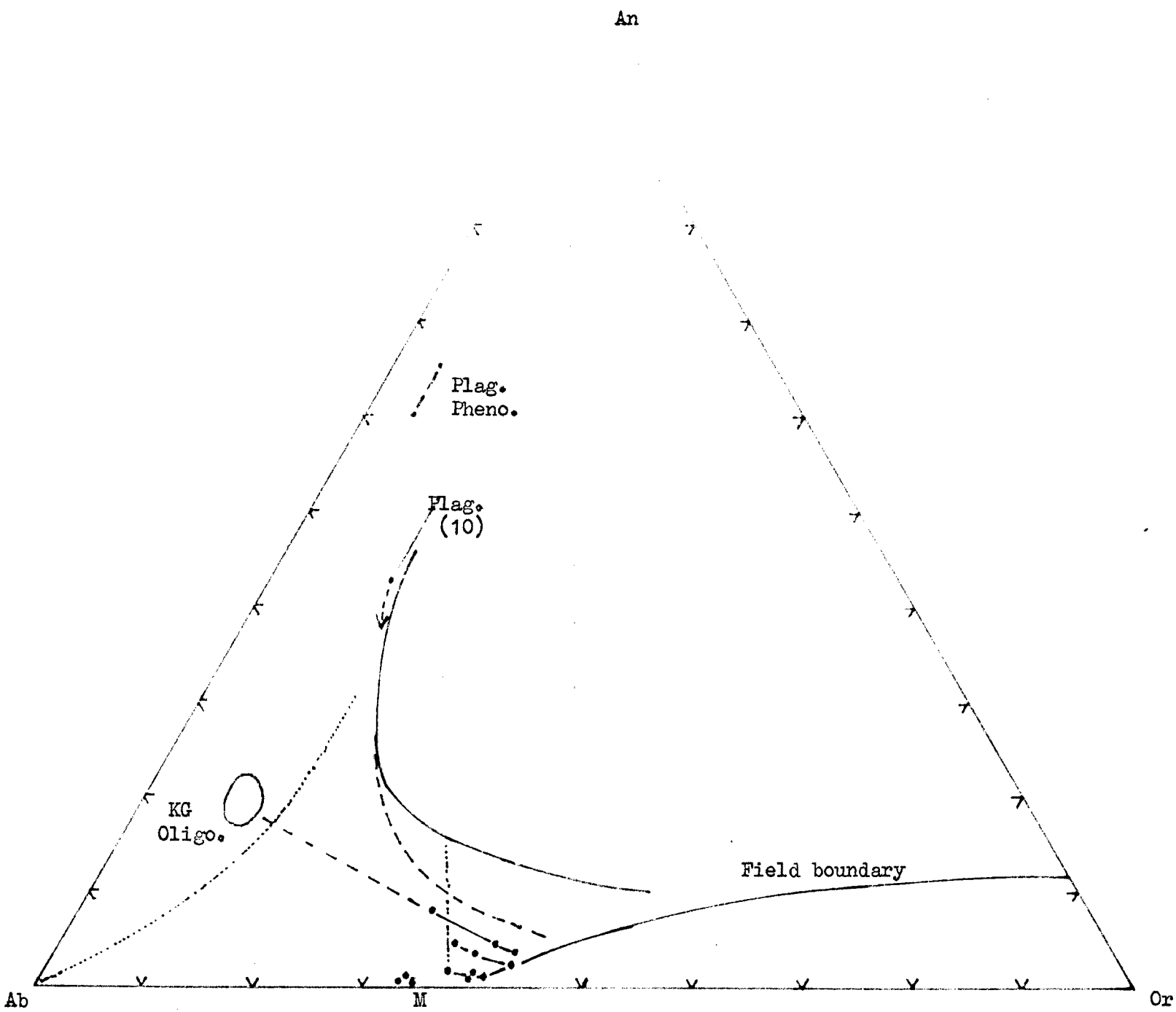

Figure 7

Compositions of analysed felspars from the trachytes and comendites, together with optical determinatio on plagioclases. Limit of solid solution of Tuttle and Bowen (1958) shown as solid line; suggested limit (see text) shown dashed. Boundaries of plagioclase, anorthoclase, and sanidine fields of composition shown dotted.

system (Carmichael, 1963). In the other field close to the An-Ab and Ab-Or joins only one felspar crystallises, and the field is known as the one felspar field.

The extent of ternary solid solution being a temperature dependent property, Tuttle and Bowen have produced a diagram showing this varying extent of solid solution between An, Ab, and Or, and its fall with temperature reduction (op. cit., Fig. 66). Tuttle and Bowen (op. cit.) further state that silica, nepheline, and water are the principal causes of temperature lowering in salic rocks, and hence more limited ternary solid solution in the felspars.

A plot of the normative felspar components An, Ab and Or for the Nandewar rocks (Fig. 8) shows that for the basaltic and trachyandesitic rocks with plagioclase as a significant normative component, the extent of ternary solid solution in the felspars approximates that shown by Tuttle and Bowen (1958, Fig. 64), but when the felspars approach the minimum melting composition on the Ab-Or join, the extent of ternary solid solution is much smaller (from the composition of the alkali felspar fractions, Fig 7), and the ternary solid solution curve approximates that shown by Turner and Verhoogen (1960, Fig. 11) and Carmichael (1960b). This falling extent of ternary solid solution in the felspars is due to falling temperature with differentiation. The curve showing the assumed limit of ternary solid solution in the felspars in the system An-Ab-Or for the Nandewar alkaline rocks is shown in Fig. 8 .

The course of felspar fractionation has been traced in the Nandewar alkaline rocks in Fig. 7 .

In the 'big felspar' basalts and the olivine basalts, the first

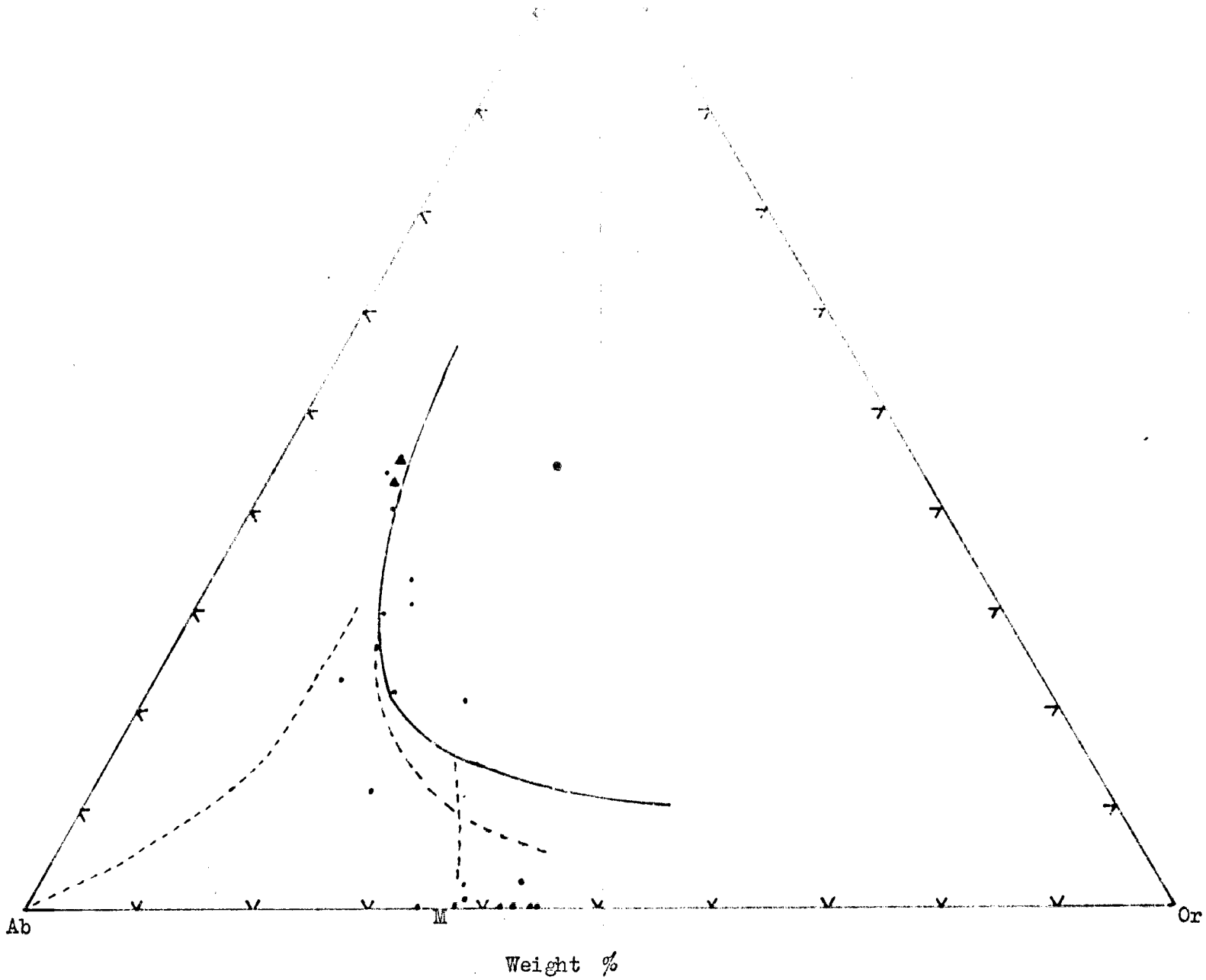

Figure 8

Bulk normative felspars of analysed rocks. Permian calc-alkaline andesites, triangles, contact teschenite, large circle. Limits of solid solution as in Fig. 7. M is the minimum melting composition.

crystallised plagioclases (the cores of the phenocrysts) have compositions ranging from An_{65} to An_{60}, and by reaction with the magma, which becomes richer in the Ab component by the removal of calcic plagioclase, the crystals form zones progressively enriched in Ab, the composition of the outer zones approaching An_{45-50}. These phenocrysts do not have appreciable amounts of Or, and the bulk of the potash in the rocks (up to 10-15 per cent of the Or component in the An-Ab-Or system in the bulk normative compositions, Fig. 8) occurs in the groundmass plagioclases, which have a composition of An_{40}.

In the trachyandesites, the bulk normative composition of the rocks in the system An-Ab-Or (Fig. 8) show that these felspars are much richer in potash. Rare plagioclase microphenocrysts, where they occur, have compositions ranging from An_{60} to An_{40}, and the groundmass plagioclases, which make up the bulk of the rock, range from An_{40} to An_{35}. A measurement of $\bar{2}01$ X-ray peaks in the felspars from the trachyandesite 10 gives an Or content of 11 per cent, and, as mentioned before, the bulk normative felspar components in the trachyandesites 8A and 15 (which are rather similar to those from the mugearites of Muir and Tilley, 1961, Fig. 6) show that these plagioclases must have much more Or in solid solution, and calcic anorthoclase is undoubtedly present. The trends for the felspar crystallisation in these rocks are shown in Fig. 7 .

The felspar fractionation in the basalts and trachyandesites consists of the plagioclase becoming more sodic, with slight enrichment in potash to produce potash oligoclases. Since the bulk normative felspar components do not enter the two felspar field, only one felspar is precipated, although lack of equilibrium gives, by zoning, various members of the differentiation sequence in any one rock.

Rather rapid changes of felspar compositions then occur in the so-called

two felspar trachytes. As explained before, these two felspar trachytes have not been named in the sense of Carmichael (1963); indeed the bulk normative felspar components never enter the two felspar field. Rather, due to the lack of attainment of equilibrium in these rocks, both plagioclase and alkali felspar are present in the trachytes although both are zoned. Using the terminology of Carmichael (1963), these felspars all belong to the single plagioclase-anorthoclase solid solution series.

In the trachyte KG a plagioclase of composition $An_{20}Ab_{71-68}Or_{10-12}$ is accompanied by anorthoclase with about 12 per cent An, and both these felspars are rimmed with alkali felspar. Chemical analyses of the felspar fractions from this rock reveal fractions with successive compositions $An_8Ab_{58}Or_{34}$, $An_4Ab_{56}Or_{40}$, and $An_{3.5}Ab_{54.3}Or_{42.2}$ (Fig. 7). The last fraction is very close to the bulk normative felspar composition $An_{2.4}Ab_{55.6}Or_{42.0}$. In the anorthoclases, cross-hatched twinning is seen, a feature which is only detected in sodic anorthoclases (Smith and MacKenzie, 1958), so that the composition of the anorthoclase phenocrysts must lie between that of the potash oligoclase and the chemically analysed fractions.

Analysed felspar fractions from the comendite 73-5 show a range in composition of from $An_4Ab_{60}Or_{36}$ through $An_3Ab_{59}Or_{38}$ to a final composition of $An_2Ab_{56}Or_{42}$ (Table 23).

All the felspars so far discussed from the trachytes reveal enrichment in Or relative to Ab, with falling amounts of An. All the bulk felspar compositions lie within the one felspar field. When the liquids precipitating the felspars reach the composition of the most differentiated felspars just discussed from the trachyte KG and the comendite 73-5, they reach the cotectic, or the boundary curve (Carmichael, 1963) which is the curve separating the fields of crystallisation of plagioclase and alkali felspar

in the system An-Ab-Or (Tuttle and Bowen, 1958). Strictly speaking, this boundary curve only separates the fields of plagioclase and alkali felspar in hydrous systems, as in anhydrous systems the boundary curve has quite a different orientation, and separates fields of leucite and felspars (Franco and Schairer, 1950), but the field of leucite contracts rapidly and soon disappears with increasing pressure of water (Bowen and Tuttle, 1950). This boundary curve proceeds from the Or-An join (at approximately $Or_{88}An_{12}$) towards the Ab-Or join, approaching closer to the join and eventually ending at approximately $Ab_{65}Or_{34}An_{1}$. Carmichael (1963) has emphasised that this boundary curve does not reach the Ab-Or join.

When the liquids reach the boundary curve, felspars precipitated are progressively enriched in Ab relative to Or, with falling An, since the boundary curve is the locus of points representing liquids existing at falling temperatures in moving from the An-Or join towards its termination near the alkali felspar minimum at $Ab_{65}Or_{35}$ on the Or-Ab join.

The analysed felspar fractions from the trachytes 24 and GOV4 and from the comendite 73-12 (Table 24) help to define this boundary curve (Fig. 7). The two felspar fractions from the trachyte 24 may lie on either side of this boundary curve, although the compositions are not markedly different. The final felspar compositions are represented by those from the comendite 73-12, and these mark the end of the boundary curve in the An-Ab-Or system, and are also very close to the alkali felspar minimum $Ab_{65}Or_{35}$ on the Ab-Or join (Fig. 7).

Carmichael has stated that it is incorrect to consider the felspar relationships of natural acid liquids solely in terms of the felspar

components, as the presence of quartz will have a great effect on the position of the alkali felspar minimum (1963, p. 103). Stewart and Roseboom (1962) however state that for compositions in the system Or-Ab-An-Qtz, the felspar relations in the An-Ab-Or system can be quite faithfully represented by projection onto the felspar plane from the quartz-bearing system, but that for the liquids, projection will not represent the true relations, as the extra component will move the compositions outside the felspar plane into the An-Ab-Or-Qtz tetrahedron.

In the system Qtz-Or-Ab, a thermal valley extends from the alkali felspar minimum on the Ab-Or join to a point slightly to the Ab-Qtz join side of the ternary minimum on the quartz-felspar boundary curve (Tuttle and Bowen, 1958; Carmichael, 1963). Carmichael and MacKnezie (1963) have proposed that this valley is a unique fractionation curve, and that liquids whose compositions lie close to this valley will, with perfect fractionation, move asymptotically towards the valley until they reach the quartz-felspar boundary, and further that no liquid can cross this valley or move out of it with fractionation.

The liquids moving down this thermal valley with falling temperature towards the quartz-felspar boundary will precipitate felspars with increasing Or/Ab ratios as the amount of quartz increases and as the composition of the liquid moves away from a simple Ab-Or binary mixture (Tuttle and Bowm, 1958).

These findings are borne out by a study of the Nandewar alkaline rocks. The bulk normative compositions of the rocks, in terms of Qtz, Ab, and Or, have been plotted in Fig. 9 (only those rocks with more than 80 per cent of the normative components Qtz, Ab, and Or have been plotted). For those rocks with the greatest amounts of normative Qtz (100-6, Mt. L, Mt. W, and

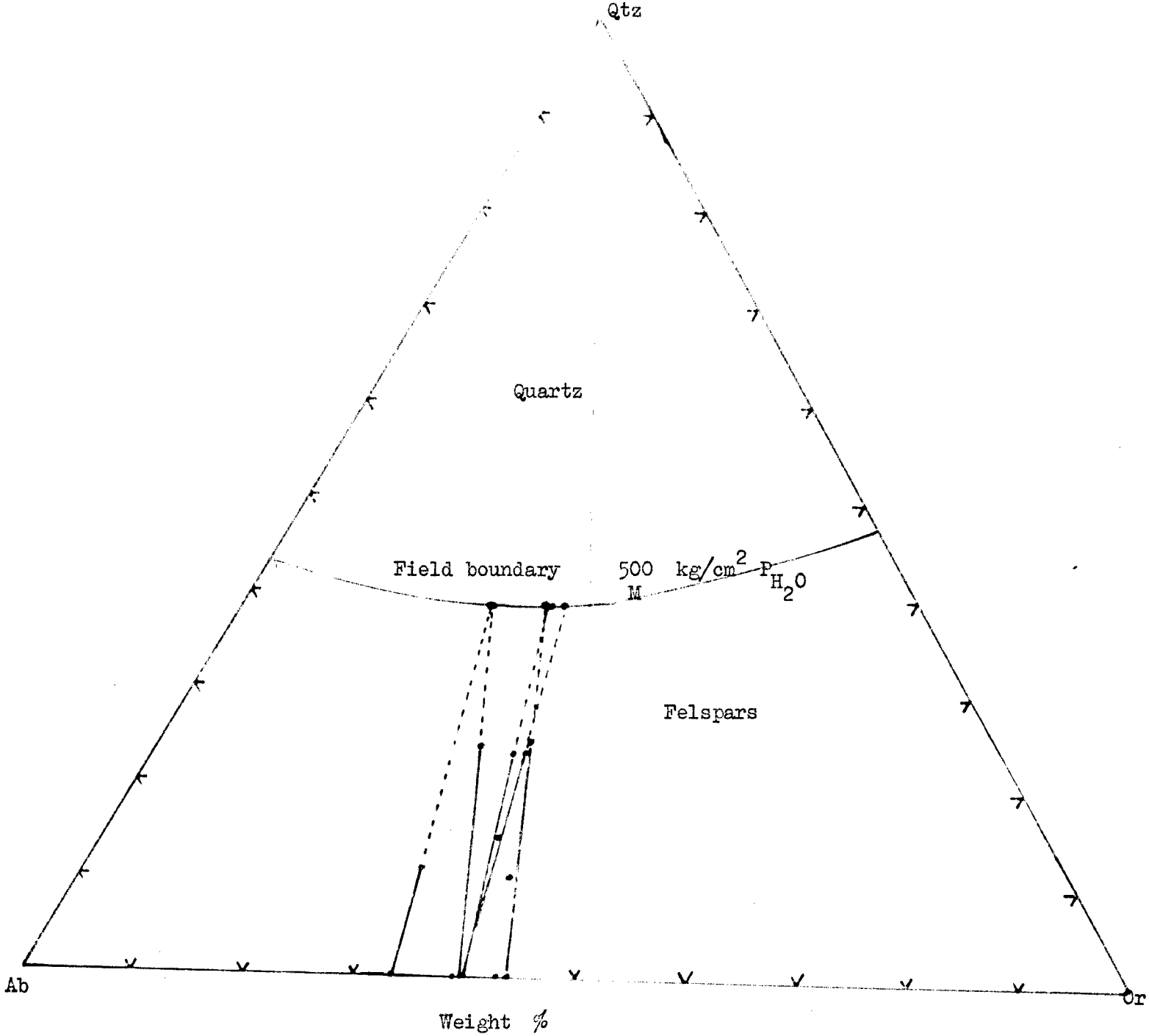

Figure 9

Plot of trachyte and comendite compositions in terms of Qtz, Ab and Or, linked by tie lines to felspar compositions on the Ab-Or join. The quartz bearing rocks have had the tie lines produced to the quartz-felspar boundary, to an assumed residual liquid (see text). M is the minimum on the boundary surface at the water pressure shown (Tuttle and Bowen, 1958).

104-E), the felspar compositions are more Or rich than the alkali felspar minimum of $Ab_{65}Or_{35}$ in the Ab-Or system. The compositions of the felspars of these rocks (from $\bar{2}01$ X-ray measurements, Table 22) are: Or_{40} - 100-6; Or_{39} - Mt L; Or_{44} - Mt W; and Or_{40} - 104-E.

Tie lines between the felspars (plotted on the Ab-Or join) and the bulk normative compositions of the rocks in the system Qtz-Ab-Or have been drawn in Fig. 9 . These tie lines have been produced in a straight line to meet the quartz-felspar boundary for the quartz bearing porphyritic rocks (73-12, Mt L, 104-E, Mt W). The points at which these tie lines meet the quartz-felspar boundary (at 500 kg/cm^2 water pressure) approximate the composition of the residual liquids. The trend of these tie lines reveal the trend of the thermal valley (Carmichael and MacKenzie, 1963) in the Qtz-Ab-Or system, and shows that it intersects the quartz-felspar boundary on the Ab-Qtz join side of the ternary minimum on this boundary (Carmichael, 1963).

The position of the thermal valley for the unusual peralkaline pantellerites and comendites has been studied by Carmichael (1962) and Chayes and Zies (1962), both of whom considered felspar fractionation and residual liquids in the Qtz-Ab-Or system, and drew tie lines between the felspars, total rock compositions, and residual liquids in this system. They found unusual trends for the thermal valley in peralkaline rocks, and Carmichael and MacKenzie (1963) have presented experimental evidence on this problem. The basis upon which Carmichael and MacKenzie drew their conclusions has been criticised by Bailey and Schairer (1964) and also by Chayes (1964).

Briefly, Carmichael (1962) showed that for natural pantellerites with a molecular excess of alkalies over alumina, the thermal valley in the system Qtz-Ab-Or was shifted towards the Or-Qtz sideline with increasing

peralkalinity (op. cit., Fig. 6), thus giving the association of relatively sodic felspar phenocrysts with potash enriched liquids. Carmichael and MacKenzie (1963) showed that by adding progressively greater amounts of ac and ns to synthetic mixtures in the system Qtz-Ab-Or, the same shift in the thermal valley as observed by Carmichael (1962) for natural rocks, could be produced.

Bailey and Schairer (1964) have stressed that if ac and ns are added to composition in the system Qtz-Ab-Or, the compositions of the liquids cannot be projected onto the Qtz-Ab-Or plane. The normative calculation used in constructing the liquid compositions in the system arbitrarily assigns all the K_2O to Al_2O_3 to make felspar, and all the peralkalinity is expressed in terms of ac and ns which are not plotted in the Qtz-Ab-Or system, and this distorts the actual relations present (Bailey and Schairer, 1964).

Chayes (1964) has shown that for two pantellerites, the tie lines in the system Qtz-Ab-Or between the alkali felspar phenocrysts and residual liquids do have the trend postulated by Carmichael (1962) if the CIPW norm conventions are adhered to, but if the Na_2O and K_2O, after an equal amount of Na_2O is allotted to Fe_2O_3 to form ac, are then allotted without preferential partition to felspar, metasilicate, and chloride molecules, the trend of the thermal valley is radically changed, so that the residual liquids are actually impoverished in K_2O with respect to the alkali felspar phenocrysts (Chayes, 1964, Fig. 71), a feature also noted by Bailey and Schairer (1964, Tables 1 and 2).

Although the trachytes and comendites in the Nandewars are peralkaline, they are not strongly so (the maximum molecular ratio $\frac{Na_2O + K_2O}{Al_2O_3}$

is 1.14), and using the CIPW norm conventions in the calculations, the tie lines in the Qtz-Ab-Or system between the bulk compositions and alkali felspar phenocrysts show no preferential enrichment in either Na_2O or K_2O in the liquids. The results for the Nandewar peralkaline trachytes and comendites agree very closely with those of Chayes (1962) for the comendites from Le Commende and Le Fontane, Isola San Pietro, Sardinia, which are also mildly peralkaline. Chayes (op. cit.) has contrasted these with the trends for strongly peralkaline pantellerites from Pantelleria.

It would appear that for alkaline series which are only mildly peralkaline, the residual liquids show no preferential enrichment in either K_2O or Na_2O with respect to the alkali felspar phenocrysts, but that for strongly peralkaline rocks (pantellerites) the residual liquids are preferentially enriched in Na_2O with respect to the alkali felspar phenocrysts due to the operation of the "orthoclase effect", in which K_2O preferentially combines with the Al_2O_3 to form orthoclase in the phenocrysts (Bailey and Schairer, 1964; Chayes, 1964).

CHEMISTRY

METHODS OF ANALYSIS

Wet chemical methods: Classical methods were used for SiO_2, CaO, and MgO following Washington (1930); fusion with Na_2CO_3 and dissolution in HCl, followed by the separation of the silica. The CaO was determined by separating the insoluble oxalate, and the magnesium was determined as the pyrophosphate. After weighing, the magnesium pyrosphosphate was dissolved in 1:1 H_2SO_4, and the Mn in the precipitate was determined colorimetrically. The Mn, computed as manganese pyrophosphate, was subtracted from the Mg.

FeO was determined by dissolving the sample with excess ammonium metavanadate in HF and back titrating with standardised $Fe(NH_4)_2(SO_4)_2$.

Al_2O_3 was determined by dissolving the sample in HF, and then precipitating the $R_2^{3+}O_3$ group in alkaline solution. After redissolving, the Al_2O_3 was separated in an ion exchange column. The Al was reprecipitated with NH_4OH, and determined as Al_2O_3, deducting P_2O_5 and TiO_2.

Na_2O and K_2O were determined on the flame photometer using an oxy-hydrogen flame, after the removal of Ca, Fe, and Al, which were precipitated with ammonia and $CaCO_3$ in order to remove any interference from these ions (Cooper, 1963). Standards were made up in a 2 per cent ammonium sulphate solution to obtain the same concentration of NH_4^+ and SO_4^{2-} as in the unknown solutions (Shapiro and Brannock, 1956).

Total Fe was determined colorimetrically using the transmittance of the orthophenanthroline complex at 5080 Å (a modification of the method of Shapiro and Brannock, 1956).

MnO was measured colorimetrically using the transmittance of the permanganate at 5242 Å, and the TiO_2 was measured by the transmittance

of the 1:2 dihydroxy-benzene 3:5 disulphonic acid ('Tiron') complex at 4300 Å. P_2O_5 was determined by measuring transmittance at 4300 Å by a solution containing the molybdivanadophosphate complex (Shapiro and Brannock, 1956).

X-ray spectrographic methods of analysis:

The major elements Fe, Mn, Ti, Ca, K, Al, P, and Si were determined by the X-ray spectrograph.

The methods used in this study are those developed by Dr. Norrish, of the C.S.I.R.O. Adelaide, and Mr. B.W. Chappell, of this department, and are outlined briefly here.

Special methods of specimen preparation are needed for these determinations. A summary of the general theory of X-ray spectrochemical analysis has been presented by Parrish (1956).

The wavelength of X-rays emitted by a sample increase with decreasing atomic number (Parrish, op. cit., p. 270, Fig. 3). The effect of using long wavelength X-rays is that only the surface layer of a sample is penetrated and excited by the incident X-rays (only 5μ are penetrated for Al radiation). Hence particle size of the sample is most important, and it is necessary to fuse the sample in a suitable flux to eliminate particle effects.

The flux used was made up of lithium tetraborate (lithium has too low an atomic number to absorb the X-rays of the wavelengths used), lithium carbonate to lower the fusion temperature, and a heavy absorber, lanthanum oxide. The presence of this heavy absorber reduces the effects of mass absorption and emission of elements other than those being measured,

as it 'swamps' the effects of other elements because it has a high mass absorption coefficient itself.

The proportions of material used in the fusion mixture are:

0.04 mole	La_2O_3	13.03 gm.
0.2 mole	$Li_2B_4O_7 5H_2O$	51.84 gm.
0.4 mole	Li_2CO_3	29.55 gm.

The mixture is fused in graphite crucibles at 1100° - 1200°C for 20 minutes, broken into cubes after cooling, and ground in a tungsten carbide 'Sieb' mill for 3 minutes to bring the grainsize down to about 2-3 μ.

For each unknown sample, the following quantities were taken:

1.5000 gm fusion mixture

0.0200 gm $NaNO_3$.

0.2800 gm unknown sample.

This is thoroughly mixed, fused at about 900°C in a gold-lined Pt crucible, mixed while molten, then poured onto a graphite disc and compacted into a circular button with an Al piston. The $NaNO_3$ is added to the mixture to prevent the fusion mixture attacking the gold in the crucible. The "buttons" are finally annealed on asbestos pads.

The buttons were then analysed by X-rays emission spectrography. The equipment used for these analyses was manufactured by Philips, and consisted of a PW 1010 H.T. generator (stabilised), PW 1050 goniometer with flow proportional and scintillation counters, PW 1520 specimen holder, and PW 1352 transistorised pulse height analyser, timer/counter, recorder

and printout combination.

The specimens were placed in the specimen chamber and bombarded with X-rays. The emitted X-rays from the specimen were analysed by a crystal of known d spacing, giving fixed angular settings for the radiation of differing wavelengths according to the Bragg equation:

$$n\lambda - 2d \sin \theta$$

The pulses were counted, and subjected to pulse height analysis, to select pulses from the specimen and eliminate background pulses. These pulses were counted for either a fixed time or for a fixed number of counts.

Short details of X-ray tubes, analysing crystals, and collimators used are listed below;

Cr tube	44kV22mA	For the light elements - all elements lighter than Ti - Ca, K, P, Si, Al.
W tube	40kV20mA	For Mn and Fe.
Collimators	Coarse collimator, 480mμ.	
Analysing crystals	LiF	2d = 4.028 Å Used for Fe, Mn, Ti, Ca.
	PET	2d = 8 Å Used for K, P, Si, Al.
Vacuum	For all elements lighter than, and including K. (K, P, Si, Al and also for Ca and Ti).	
Counters	Scintillation counter: Elements heavier than Ti. In practice for most of the major elements, the proportional counter was used, because for Fe and Mn an excessive operating voltage is needed on the scintillation counter (1600 V). Proportional counter: Necessary for all elements analysed in a vacuum.	

Internal drift was overcome by counting a silicate mix standard, made up by Mr. Chappell (after Dr. Norrish). This was designed to give a count of from 15,000 counts per second to about 50,000 c.p.s. for the major elements. The time taken to accumulate 10^6 counts on it was determined before and after each 3-4 unknown determinations.

The heavy elements, which usually give high count rates, were counted for 40 seconds, while the lighter elements with low count rates were counted for 100 seconds. Counting statistics show that the standard deviation σ of N counts is :

$$\sigma = \sqrt{N}$$

For the 95 per cent confidence level :

$$2\sigma = \frac{2}{\sqrt{N}}$$

Thus for a Ca value of 5 per cent 100 second counts give 2σ = 0.17 per cent, 0.008 per cent Ca.

Al 100 second counts give 2σ = 0.2 per cent

Mg 100 second counts give 2σ = 0.7 per cent

Broadly the counting error is :

For heavy elements with 40 second counts, 0.01 per cent of element
light " " 200 " " 0.05 per cent " "

Each specimen is usually counted in duplicate but some are counted three times. This eliminates accidental errors and spurious pulses.

The sensitivity, which is taken to be 3 times the standard deviation of the blank, is: for Fe - Mn 0.001-0.002 per cent, P 0.02 per cent, Si, Al 0.03 per cent, Mg 0.5 per cent and for Na 1 per cent.

The final precision and reproducability is expected to be:

Better than 1 per cent for elements heavier than K

2 per cent for P and Si

5 per cent for Mg

After counting each sample, corrections are made for instrumental dead time, resulting in an increase of the actual counts per second, especially for high count rates. When counting a fixed count, correction is simply achieved by subtracting from the time for this count, the dead time (which for the Philips equipment described above is 2.9 μ secs per count, which is 2.9 seconds per 10^6 counts), and calculating counts per second. For fixed time counts, the correction is achieved according to the relation:

$$N' = \frac{N}{T - \mu N}$$

where: N = recorded numbers of counts

T = time taken

μ = dead time

N' = actual counts per second

The count rates of the silicate mix before and after the counting of the unknowns were averaged, and normalised to an even figure throughout (say average count rate was 18342 counts per second, normalise to 18000). The counts per second of the unknowns were also normalised in the same ratio. This procedure countered instrumental drift.

The linear factor giving the approximate percentage of each element from the counts per second was obtained from the measurement of standard samples whose composition and hence mass absorption coefficients were known. In general, G-1 and W-1 were used, but for some elements other analysed standards were preferred. The blank count rate was derived in each case from a button fused from spectrographically pure silica, except of course for the silica determination, where a button of spec. pure MgO was used. The blank count rate was subtracted from the standard, the modified count rate multiplied by the mass absorption coefficient, and

the factor for converting count rates to percentage composition derived from the relation between the true value of the standard and its count rate.

Mass absorption coefficient calculations: For monochromatic radiation generated at a point with an intensity I_o then at distance with intensity I the relations are:

$$\frac{dI}{I} = -\mu\, dx$$

where μ = linear absorption coefficient

$$I = I_o\, e^{-\mu x}$$

μ depends on density, $\frac{\mu}{\rho}$ = absorption coefficient, ρ = mass/unit volume

$$I = I_o\, e^{-\frac{\mu}{\rho}\cdot\rho x}$$

let $A = \frac{\mu}{\rho}$, then $\frac{AC}{p} = K$ where: K = constant

A = mass absorption coefficient

p = concentration of element

c = counts per second

For a sample consisting of many elements, the total mass absorption coefficient (for a particular wavelength) is:

$$A = \frac{w_1}{100}(a_1) + \frac{w_2}{100}(a_2) + \frac{w_3}{100}(a_3) + \cdots\cdots$$

where: w_1 = weight percent of element 1

a_1 = mass absorption coefficient of element 1 at this wave-length.

A mixture has been used for making the buttons, and a total mass absorption coefficient must be calculated for the fusion mix and $NaNO_3$, as well as for the unknown sample.

For calcium, whose $K\alpha_1$ radiation has a wavelength of 3.360 Å, the mass absorption coefficient of the fusion mixture is 156.56 (mostly due to the La_2O_3), and the $NaNO_3$ has a mass absorption coefficient of 150.19. Other oxides have mass absorption coefficients at this wavelength of:

Fe_2O_3	254.2	P_2O_5	344.5
MnO	239.9	SiO_2	318.0
TiO_2	158.4	Al_2O_3	289.3
CaO	732.7	MgO	264.3
K_2O	970.7	Na_2O	232.3

If it is now assumed that the whole sample consists of the fusion mix, then the mass absorption coefficient must be corrected for the mass of the material in the button which is not fusion mix. This is done by multiplying the percentage of the total mass which each contributes by the difference between the mass absorption coefficient for the fusion mix and that for the particular constituent. If the mass absorption coefficient of a particular constituent is greater than that for the fusion mix, the difference is positive.

The following equation is then obtained:

$$A = 156.56 - 0.0111\ (156.56-150.19) + 0.001556\ (97.68 \times \text{Fe per cent}) + (83.36 \times \text{Mn per cent}) + \ldots\ldots + (75.42 \times \text{Na per cent})$$

$$= 156.49 + (0.084 \times \text{Fe per cent}) + (0.072 \times \text{Mn per cent}) + (0.002 \times \text{Ti per cent}) - (0.021 \times \text{Ca per cent}) + \ldots\ldots$$

Instead of expressing the mass absorption coefficient as an absolute number, there is some advantage in expressing it as a percentage of that obtained if the whole sample were fusion mix. Since the heavy absorber La_2O_3 has by far the greatest mass absorption coefficient in any button, the relative mass absorption coefficients will only vary by about 5 per cent - from 95 per cent - 105 per cent. This means that the values derived from each unknown before correction for mass absorption coefficients will be approximately correct, after the blank has been subtracted.

All these mass absorption calculations have been programmed and run on an IBM 1620 computer. The six or eight approximate element percentages derived by X-ray measurements, together with classical values for Na, Mg and H_2O, CO_2 were fed into the computer, which calculated the mass absorption coefficients for each element, by taking into account the values for the other elements. New values were obtained for each element after correcting for the mass absorption coefficients. Subtracting the blank readings from these values gave the true values for the elements.

For many of the analysed rocks, data has been obtained for the oxide values by both wet chemical and X-ray methods. The comparative values are set out in Tables No. 25 and No. 26 , and No. 27

It was stated earlier that the final reproducibility and precision of the X-ray silica values was expected to be better than 2 per cent. In the range of silica values found this would correspond to an error of from 1 per cent to about 1.4 per cent in silica. On comparing the classical and X-ray silica values, it can be seen (Table 26) that in only some of the specimens studied, does the discrepancy between the values derived by the two methods approach this amount. The greatest difference between the two

TABLE 25

COMPARISON OF VALUES FOR ELEMENTS DETERMINED BY X-RAYS AND BY CLASSICAL WET CHEMICAL METHODS

Rock No.	MnO		TiO_2		K_2O		P_2O_5	
	Chem.	X-ray	Chem.	X-ray	Chem.	X-ray	Chem.	X-ray
5P	0.09	0.15	2.39	2.40	1.68	1.43	0.64	0.74
10	0.08	0.13	2.76	2.76	2.28	1.81	1.04	1.04
BG	0.17	0.20	1.68	1.80	4.16	3.36	0.88	0.95
8A	0.13	0.21	1.77	1.80	3.39	3.19	0.97	0.95
151-3A	0.08	0.10	1.18	1.14	1.26	1.24	0.74	0.40
151-3	0.08	0.11	1.12	1.09	1.43	1.15	0.51	0.36
118-2	0.09	0.15	1.46	1.49	3.80	3.07	0.53	0.52
KG	0.15	0.16	0.82	0.77	5.37	5.26	0.59	0.31
151-2	0.08	0.14	0.42	0.41	5.83	5.57	0.22	0.13
GOV4	0.12	0.14	0.34	0.34	5.32	5.17	0.02	0.05
73-5	0.01	0.003	0.31	0.29	6.23	6.11	0.12	0.11
73-12	0.00	0.00	0.05	0.12	5.84	5.00	0.00	0.02
104-E	0.04	0.001	0.27	0.26	5.30	5.35	0.10	0.12

TABLE 26

COMPARISON OF VALUES FOR ELEMENTS DETERMINED BY X-RAYS AND BY CLASSICAL WET CHEMICAL METHODS

Rock No.	SiO_2		CaO		Al_2O_3		Total Fe as Fe_2O_3	
	Chem.	X-ray	Chem.	X-ray	Chem.	X-ray	Chem.	X-ray
CTS	45.20	44.81						
E7	47.51	47.42	9.15	9.28				
5P	48.17	47.98	9.70	9.76	17.67	17.53	9.75	9.72
Gr1	49.31	48.43	7.73	7.83				
10	49.30	49.12	8.47	8.58	17.60	17.11	10.80	10.43
15	50.35	50.69	6.73	6.68				
E8	51.68	50.40	7.46	7.43				
BG	52.63	53.36	5.04	5.10	15.80	16.04	10.27	9.85
8A	53.76	53.90	5.44	5.16	16.02	16.27	11.03	10.29
151-3A	55.47	55.43	7.46	7.45	17.45	17.76		
151-3	56.23	55.88	7.92	7.84	17.71	17.40	6.77	6.93
118-2	56.42	56.66	5.14	5.06	16.93	17.01	7.95	8.10
KG	60.14	59.70	2.73	2.76	16.32	17.07	6.06	5.94
151-2	62.90	62.69	2.04	1.83	16.17	16.15	4.82	4.80
24	65.59	65.73	0.73	0.36				
GOV4	68.26	68.12	0.88	0.68	14.28	13.95	4.23	5.07
73-5	66.53	66.13	0.50	0.61	19.08	18.76	0.87	0.53
73-12	70.21	70.62	0.08	0.09	16.81	16.46	0.95	0.90
100-6	72.98	72.70						
Mt W	72.99	73.45						
Mt L	73.46	74.10	0.40	0.04				
104-E	73.82	74.04	0.51	0.11	14.39	14.31	0.71	0.68
24 Coss.	40.74	41.27						
T1 tibiot	36.57	36.15						
P1px	49.39	49.39						
GOV4px	49.99	49.32						
5Ppx	49.64	49.56						

TABLE 27

COMPARISON OF VALUES FOR ELEMENTS DETERMINED BY X-RAYS AND BY CLASSICAL WET CHEMICAL METHODS

(Chemical values by Dr. White, X-ray values by M.J. Abbott)

	P_2O_5	
	Chem	X-ray
CTS	0.72	0.73
E8	0.98	0.92
Gr 1	0.71	0.75
E7	0.94	0.93
15	1.37	1.30
24	0.09	0.07
100-6	0.04	0.04
Mt L	0.01	0.08
Mt W	0.04	0.07

sets of values is about 1.3 per cent, and for most of the determinations the agreement is much better than this. It seems from this work that the actual error of silica determinations by the X-ray method can be better than 0.8 per cent.

For the alumina determinations, the error between the classical and X-ray determinations is 2 per cent in some cases. Assuming that where the difference between the two values is 2 per cent, each value (classical and X-ray) is out by 1 per cent, it can be stated that the error of alumina determinations by X-rays should be better than 1 per cent.

In the case of calcium determinations, the greatest error between the classical and X-ray values is about 1 per cent to 1.3 per cent, except in the lower values, where sometimes the classical values are anomalously high. These high values appear to be due partly to the Ca contributed by the reagents (especially sodium carbonate). The error of X-ray determination of calcium should be better than about 1 per cent.

The agreement between the classical and X-ray P_2O_5 values is quite good, but again some of the classical values are anomalously high. It has been found (Shapiro and Brannock, 1956), that, especially where the Fe_2O_3 is high, the molybivanadatophosphate colorimetric method of measuring P_2O_5 will give high values, because the ferric iron contributes to transmittance of the solution at 4300 Å.

A further series of P_2O_5 determinations were carried by Dr. A.J.R. White, on solutions prepared by the present author, and these results are compared with the X-ray values in Table 27 . Again, the agreement between the two sets of values is quite fair, apart from two very low values, for which the X-ray values are much higher.

Because the classical K_2O determinations carried out on the flame photometer are not regarded as reliable, no inferences can be made regarding the relative accuracy of the X-ray and flame photometric methods of determining K_2O. However, all the flame photometer figures are higher than the X-ray values, pointing to some systematic error.

The agreement between the classical and X-ray values for TiO_2, is, except for two or three cases, within 1 per cent.

The values of MnO derived by colorimetric methods are systematically lower than the X-ray values. However, MnO is low in all cases, and the higher X-ray values are due to the choice of a blank. If a higher blank is chosen, some of the values are negative, but a blank higher by about 0.02 per cent would give better agreement between the two sets of values.

The iron values (expressed as Fe_2O_3) do not show very good agreement between the two methods of determination. Less confidence can be placed in the orthophenanthroline colorimetric values at high Fe concentrations because of dilution errors in the preparation of the sample for colorimetry.

In the final statement of analyses for the rocks and minerals, classical values were taken for SiO_2, FeO, MgO, Na_2O, and H_2O, whereas for the other oxides the X-ray values were preferred.

Trace Elements:

The trace elements Rb, Sr, Zr, and Ba have been determined in the rock samples by X-ray fluorescence, using different methods than those for the major elements.

The samples for analysis were prepared by pressing about 2 grams of the finely ground rock powder into a button, reinforced by a backing of boric acid.

Because the peak/background ratio of the trace elements is much lower than for the major elements, the background must be determined for each sample. This was achieved by measuring the background a fixed angular distance both above and below the peak. The background counts/second were then averaged and subtracted from the peak counts/second. This assumes that the background either increases or decreases linearly between the angular settings used for eading the background. However, the background reading is not a linear function of angular setting (this is found by running an optical grade silica disc over the angular range involved). A correction must be made for the background curvature.

In the Rb and Sr determinations, the respective Kα peaks are 1.48° 2θ apart, and these peaks interact with each other to a certain extent. The procedure used for the measurement of these elements is as follows: The peak positions are established by running a standard Rb-Sr sample. This sample is also run on the Rb and Sr peaks between 3 - 4 unknown determinations to correct for instrumental drift, as for the major elements (pages 153-154). Having found the Rb and Sr peaks, the background is read 0.74° 2θ below the Sr peak, a similar distance above it (this is also 0.74° 2θ below the Rb peak), and 0.74° above the Rb peak. The Sr and Rb peaks are also read. These readings are converted to counts per second after dead time corrections, and the backgrounds are averaged and subtracted from the peaks which they bracket. To correct for background slop:

1.52 per cent background is added to Sr peak

0.84 per cent " " " " Rb peak

To correct for the tail effects of Rb peak on Sr, and vice versa:

1.07 per cent of Rb peak added to Sr peak

0.67 per cent " Sr " " " Rb "

The tail effects have been calculated by running a sample of finely ground silica (1) Alone; (2) With 1000 ppm Rb; (3) With 1000 ppm Sr. (1) gives background; (2) gives effect of Rb on Sr; (3) gives effect of Sr on Rb. For the Rb, Sr, and Zr determinations, the mass absorption coefficients were measured directly. A known mass of rock material was pressed into a hole in a perspex slide, the hole being of known area. The intensity of radiation given off by a sample of the particular element concerned was measured at the appropriate angular settings, without the rock sample in front of the scintillation counter, and again with the sample in front of the counter. The ratios of I/I_o (see page 155 for definitions of terms) can then be calculated. Knowing the mass of the sample, and its area, and assuming a constant thickness, the density can be calculated. The mass absorption coefficient (A) can then be calculated from the function:

$$A = \ln \frac{I_o}{I}^{\frac{1}{e}}$$

and the concentration of the element can be determined from the relation:

$$\frac{AC}{p} = K \text{ (cf. page 155)}$$

The mass absorption coefficients for Ba were calculated, using the known composition of the rocks.

G-1 and W-1 were used to derive the calibration constants for each

element. The following values were used: (all expressed in ppm)

	Rb	Sr	Ba
G-1	210	247	1220
W-1	22	186	225

The Ba values are based on those of Fleischer and Stevens (1962); the Rb and Sr values are based on isotope dilution determinations (Geophysics Department, A.N.U.).

Brief details of tubes, crystals and counters used:

W tube		Zr	
Cr tube	54kV18mA	Ba	
Mo tube	54kV18mA	Rb and Sr	
Collimators	Coarse collimator, 480 mμ		Ba
	Fine collimator, 160 mμ		Rb, Sr, and Zr.
Crystal	LiF 2d = 4.028 Å for all trace elements		
Counters:	Flow proportional counter for Rb, Sr, and Zr.		
	Scintillation counter for Rb, Sr, and Zr.		

A vacuum was used for analysing Ba, because the long wavelength $L_{\beta 2}$ line was used. With the equipment in use, the voltage needed to excite the Ba K line could not be attained.

The sensitivity of the trace element determinations was about 1 ppm for Rb and Sr, while for Ba it was 10 ppm, and for Zr it is about 5 ppm.

Because of the relatively high effects of the Rb peak on the Sr peak, any results in which the ratio of Rb:Sr is greater than 10:1 are not believed to have as high a precision as the other results.

CHEMISTRY OF THE ALKALINE ROCKS

MAJOR ELEMENTS

The chemical analyses and C.I.P.W. norms of the alkaline rocks are set out in Tables 29 to 34 inclusive, and analyses of two Permian calc-alkaline andesites and the chilled contact teschenite are set out in Table 35, and the norms of these rocks are in Table 36. The rock numbers, petrographical types, modes of occurrence and localities are indexed in Table 28.

In each of the tables of chemical analyses the Kuno Solidifation Index $\left(\frac{MgO \times 100}{MgO + FeO + Fe_2O_3 + Na_2O + K_2O}\right)$ after Kuno et al. (1957); the Larsen index ($1/3\ SiO_2 + K_2O - FeO - MgO - CaO$) after Larsen (1938); and the peralkalinity ratio where appropriate (molecular $\frac{Na_2O + K_2O}{Al_2O_3}$) have been calculated and tabulated. In the tables of the norms the or, ab, an and Q, or, ab (where appropriate) ratios, recalculated to 100 weight per cent, have been set out. The weight per cent An in the normative plagioclase and the molecular ratio of $\frac{Fe^{2+}}{Fe^{2+} + Mg}$ in the normative ferromagnesian minerals are also tabulated.

The most noticeable feature of the analyses of the series of alkaline rocks is the relatively differentiated nature of the olivine basalts. The most basic olivine basalt (Gr 1) has a Kuno S.I. of 31.5. Rocks with a Kuno S.I. less than 35 are partly differentiated; Kuno et al. (1957) state that the parental alkali olivine basalt magma in Hawaii has a S.I. ranging, in general, from 45 to 35. In the absence of more basic olivine basalts in the saturated alkaline series in the Nandewars, the olivine basalt Gr 1 will be considered the 'parent' magma, even though differentiated to

TABLE 28

INDEX OF ANALYSED ROCK TYPES AND THEIR LOCALITIES

Rock Number and Type		Mode of occurrence	Locality
CTS	Chilled contact teschenite	Sill	Gulf Creek, east of Mt. Bobby Waa
E7	Porphyritic felspar basalt	Flow	3 miles east of Mt. Dowes, east Nandewars.
5P	Porphyritic olivine basalt	Flow	Kaputar Road, 1 mile west of Coryah Gap.
Gr 1	Porphyritic olivine basalt	Flow	Summit of Mt. Grattai.
10	Trachyandesite	Flow	Kaputar Rd, 2 miles west of Coryah Gap.
15	Trachyandesite	Flow	Kaputar Rd, 2 1/2 miles west of Coryah Gap.
E8	Porphyritic olivine basalt	Flow	3 1/2 miles east of Mt. Dowes, east Nandewars.
BG	Trachyandesite glass	Spatter Cone	Kaputar Road, 1 1/2 miles west of Coryah Gap (above flow 8A).
8A	Trachyandesite	Flow	Kaputar Road, 1 1/2 miles west of Coryah Gap (near BG).
151-3A	Andesite (Permian)	Flow	1/2 mile north of Bullawa Creek.
151-3	Andesite (Permian)	Flow	1/2 mile north of Bullawa Creek.
118-2	Alkali syenite	?	Oakey Creek, 2 miles upstream from the junction with Bullawa Creek.
KG	Two felspar trachyte	Flow	1/2 mile north Killarney Gap.
151-2	Two felspar trachyte	Dome	1 mile south Bullawa Creek.
24	Coss. Aeg-aug. Arfv. trachyte	Dome	Kaputar Road, 1 mile east of Upper Bullawa Creek turnoff.
GOV4	Coss. Hed. Arfv. trachyte	Coulee	Summit of the Governor, east of Coryah Gap.
73-5	Comendite	Dyke	1 mile north-west of Nobby's, Rocky Creek.
73-12	Comendite	Dome	1 1/2 miles north-west of Nobby's Rocky Creek.
100-6	Trachyte	Ring Dyke	Pound Mountain, Pound Creek.
Mt W	Trachyte	Dome	Mt. Waa.
Mt L	Comendite	Dome	Mt. Lawler.
104-E	Comendite	Dyke	West Fall of Killarney Gap.

TABLE 29

CHEMICAL ANALYSES OF NANDEWAR BASALTS AND TRACHYANDESITES

(all analyses by M.J. Abbott)

	E7	5P	Gr 1	10	15	E8	BG	8A
SiO_2	47.51	47.98	49.31	49.30	50.35	50.40	53.36	53.76
TiO_2	2.82	2.40	2.20	2.76	2.48	2.23	1.80	1.80
Al_2O_3	16.85	17.53	14.82	17.60	15.89	16.32	16.04	16.27
Fe_2O_3	4.25	4.06	4.27	5.12	5.92	3.84	5.71	4.75
FeO	6.71	5.09	6.40	4.78	5.07	6.35	3.73	4.99
MnO	0.15	0.15	0.16	0.13	0.17	0.17	0.20	0.21
MgO	5.62	5.27	7.45	3.03	4.10	4.96	2.73	1.89
CaO	9.28	9.70	7.83	8.58	6.68	7.43	5.10	5.16
Na_2O	3.47	3.73	3.60	4.17	4.68	4.26	4.24	5.80
K_2O	1.08	1.43	1.90	2.06	2.51	1.84	3.36	3.19
P_2O_5	0.93	0.69	0.75	1.04	1.30	0.92	0.92	0.96
H_2O^+	0.59	1.13	1.18	0.50	0.67	1.01	1.73	0.19
H_2O^-							0.10	0.06
CO_2	0.01	1.18	0.02	0.40	0.03	tr	0.10	0.80
Rb_2O	tr	tr	tr	tr	0.01	tr	0.01	0.01
SrO	0.10	0.11	0.07	0.10	0.09	0.09	0.07	0.08
ZrO_2	0.02	0.03	0.03	0.03	0.04	0.03	0.05	0.05
BaO	0.10	0.06	0.08	0.07	0.09	0.31	0.16	0.15
Total	99.49	100.53	100.07	99.67	100.08	100.16	99.41	100.12
Kuno S.I.	26.60	26.92	31.54	15.81	18.40	23.34	13.81	9.17
Larsen Index	-4.69	-2.64	-3.34	+2.10	+3.44	-0.10	+9.59	+9.07

$$\text{Kuno S.I.} = \frac{MgO \times 100}{MgO + FeO + Fe_2O_3 + Na_2O + K_2O}$$

$$\text{Larsen Index} = 1/3\ SiO_2 + K_2O - FeO - MgO - CaO$$

Localities and rock type of the specimens listed in Table 28 .

TABLE 30

C.I.P.W. NORMS OF NANDEWAR BASALTS AND TRACHYANDESITES, FROM ANALYSES LISTED IN TABLE 29. (SAME ROCK NUMBERS AS IN TABLE 29).

		E7	5P	Gr 1	10	15	E8	BG	8A
Qz					0.34			4.54	
or		6.38	8.45	11.23	12.17	14.83	10.87	19.86	18.85
ab		29.36	31.56	30.46	35.28	39.60	36.05	35.88	49.08
an		27.21	26.87	18.67	23.22	14.94	19.98	14.81	8.94
wo	di	5.30	3.88	6.33	4.18	2.97	4.54	1.61	2.23
en	di	3.69	2.96	4.55	3.53	3.28	2.98	1.39	1.35
fs	di	1.17	0.52	1.20	0.11	0.21	1.24		0.76
en	hy	5.68	5.08	4.04	4.01	2.43	3.94	5.41	0.46
fs	hy	1.80	0.89	1.06	0.12	0.15	1.63		0.26
fo	ol	3.20	3.53	6.96		3.11	3.78		2.01
fa	ol	1.12	0.68	2.02		0.21	1.73		1.25
il		5.36	4.56	4.18	5.24	4.71	4.24	3.42	3.42
mt		6.16	5.89	6.19	7.42	8.58	5.57	7.46	6.89
hm								0.57	
ap		2.23	1.65	1.78	2.46	3.08	2.18	2.18	2.27
cc		0.02	2.68	0.05	0.91	0.07		0.23	1.82
H_2O		0.59	1.13	1.18	0.50	0.67	1.01	1.83	0.25
Rest		0.22	0.20	0.18	0.20	0.23	0.33	0.29	0.29
Total		99.49	100.53	100.08	99.69	100.07	100.17	99.48	100.13
or		10.1	12.6	18.6	17.2	21.4	16.2	28.2	24.5
ab		46.6	47.2	50.5	49.9	57.1	53.9	50.9	63.8
an		43.3	40.2	30.9	32.9	21.5	29.9	20.9	11.7
Norm Plag. Wt. per cent		48.1	46.0	38.0	39.7	27.4	35.7	29.2	15.4
$\frac{100 \times FeO}{FeO + MgO}$ molec. in femics.		19.4	11.8	16.7	2.2	4.5	23.9	0.0	30.0

Localities and rock type of the specimens listed in Table 28 .

TABLE 31

CHEMICAL ANALYSES OF NANDEWAR TRACHYTES AND COMENDITES

(all analyses by M.J. Abbott).

Localities and rock type of specimens listed in Table 28 .

	118-2	KG	151-2	24	GOV4	73-5
SiO_2	56.42	60.14	62.90	65.59	68.26	66.53
TiO_2	1.46	0.77	0.41	0.41	0.34	0.29
Al_2O_3	16.93	17.07	16.15	16.45	13.95	18.76
Fe_2O_3	3.50	2.63	1.37	2.11	2.47	0.41
FeO	4.07	2.98	3.09	1.62	2.34	0.11
MnO	0.09	0.16	0.14	0.08	0.14	tr
MgO	2.71	0.78	0.61	0.14	0.07	0.11
CaO	5.06	2.76	1.83	0.36	0.68	0.61
Na_2O	5.65	4.87	6.17	7.02	6.26	6.78
K_2O	3.07	5.26	5.57	5.57	5.17	6.11
P_2O_5	0.52	0.31	0.17	0.07	0.03	0.11
H_2O^+	0.87	0.45	0.26	0.18	0.29	0.12
H_2O^-						
CO_2	0.10	1.56	0.84	0.04	0.05	0.06
Rb_2O	0.01	0.08	0.01	0.01	0.02	0.02
SrO	0.06	0.03	0.01	tr	tr	tr
ZrO_2	0.04	0.05	0.13	0.09	0.10	0.11
BaO	0.17	0.16	0.05	tr	tr	0.03
Total	100.73	100.06	99.71	99.74	100.17	100.16
Kuno S.I.	14.26	4.72	3.63	0.85	0.43	0.81
Larsen Index	+10.04	+18.79	+21.01	+25.31	+24.83	+27.46
Peralkalinity	0.75	0.80	1.00	1.07	1.14	0.95

$$\text{Kuno S.I.} = \frac{MgO \times 100}{MgO + FeO + Fe_2O_3 + Na_2O + K_2O}$$

$$\text{Larsen Index} = 1/3\ SiO_2 + K_2O - FeO - MgO - CaO$$

$$\text{Peralkalinity} = \text{molecular} \quad \frac{Na_2O + K_2O}{Al_2O_3}$$

TABLE 32

C.I.P.W. NORMS OF NANDEWAR TRACHYTES AND COMENDITES, FROM ANALYSES LISTED IN TABLE 31 . (SAME ROCK NUMBERS HAVE BEEN USED).

	118-2	KG	151-2	24	GOV4	73-5
Qz		8.68	2.35	3.34	12.46	2.71
C		2.70				0.29
or	18.14	31.09	32.92	32.92	30.55	36.11
ab	47.81	41.21	52.06	53.61	42.97	57.37
an	11.77	1.81				1.93
wo (di)	3.89		1.11	0.45	1.19	
en (di)	2.66		0.31	0.07	0.06	
fs (di)	0.92		0.85	0.42	1.28	
en (hy)	3.03	1.94	1.21	0.28	0.12	0.27
fs (hy)	1.05	2.33	3.31	1.74	2.71	
fo (ol)	0.73					
fa (ol)	0.28					
ac			0.13	5.11	7.15	
il	2.77	1.46	0.78	0.78	0.65	0.23
mt	5.07	3.81	1.92	0.50		
hm						0.41
ap	1.23	0.73	0.40	0.17	0.07	0.26
ns					0.44	
cc	0.23	3.55	1.91	0.09	0.11	0.14
H_2O	0.87	0.45	0.26	0.18	0.29	0.12
Rest	0.27	0.32	0.20	0.10	0.17	0.16
Total	100.72	100.08	99.72	99.76	100.22	100.00
Qz		10.7	2.7	3.7	14.5	2.8
or		38.4	37.7	36.6	35.5	37.5
ab		50.9	59.6	59.7	50.0	59.7
or	23.3	42.0	38.7	38.0	41.6	37.8
ab	61.5	55.6	61.3	62.0	58.4	60.1
an	15.2	2.4	0.0	0.0	0.0	2.1
$\frac{100 \times FeO}{FeO + MgO}$ molec. in femics.	20.8	47.6	67.5	82.5	94.5	0.0

Localities and rock type of specimens listed in Table 28 .

TABLE 33

CHEMICAL ANALYSES OF NANDEWAR TRACHYTES AND COMENDITES

(all analyses by M.J. Abbott)
Localities and rock type of specimens listed in Table 28 .

	73-12	100-6	Mt W	Mt L	104-E
SiO_2	70.21	72.70	72.99	73.46	73.82
TiO_2	0.05	0.13	0.26	0.25	0.26
Al_2O_3	16.46	13.20	13.44	13.91	14.31
Fe_2O_3	0.78	2.60	1.51	0.96	0.60
FeO	0.09	0.54	0.28	0.09	0.07
MnO	0.00	0.05	0.03	tr	tr
MgO	0.36	0.08	0.06	0.13	0.45
CaO	0.08	0.09	0.17	0.04	0.11
Na_2O	6.84	6.01	5.46	5.33	4.73
K_2O	5.00	4.50	5.33	5.27	5.35
P_2O_5	0.00	0.04	0.07	0.08	0.11
H_2O^+	0.47	0.31	0.32	0.18	0.12
H_2O^-					
CO_2	0.05	0.01	tr	0.04	0.03
Rb_2O	0.03	0.03	0.03	0.02	0.02
SrO	tr	tr	tr	tr	tr
ZrO_2	0.08	0.19	0.11	0.12	0.10
BaO	tr	tr	tr	tr	tr
Total	100.50	100.48	100.06	99.88	100.08
Kuno S.I.	2.75	0.58	0.47	1.10	4.02
Larsen Index	+27.87	+28.02	+29.15	+29.50	+29.33
Peralkalinity	1.01	1.12	1.10	1.04	0.95

$$\text{Kuno S.I.} = \frac{MgO \times 100}{MgO + FeO + Fe_2O_3 + Na_2O + K_2O}$$

$$\text{Larsen Index} = 1/3\ SiO_2 + K_2O - FeO - MgO - CaO$$

$$\text{Peralkalinity} = \text{Molecular}\ \frac{Na_2O + K_2O}{Al_2O_3}$$

TABLE 34

C.I.P.W. NORMS OF NANDEWAR TRACHYTES AND COMENDITES, FROM ANALYSES LISTED IN TABLE 33 . (SAME ROCK NUMBERS HAVE BEEN USED).

Localities and rock type of specimens listed in Table 28 .

	73-12	100-6	Mt W	Mt L	104-E
Qz	10.97	21.87	22.75	22.66	22.16
C					0.74
or	29.55	26.59	31.50	31.14	31.62
ab	56.83	42.85	39.46	42.21	40.02
an					
wo (di)	0.03	0.05	0.16		
en (di)	0.03	0.01	0.08		
fs (di)		0.04	0.08		
en (hy)	0.87	0.19	0.07	0.32	1.12
fs (hy)		0.69	0.06		
fo (ol)					
fa (ol)					
ac	0.92	7.06	4.37	2.55	
il	0.09	0.25	0.49	0.19	0.15
mt	0.15	0.23			
hm	0.36			0.08	0.60
ap		0.10	0.17	0.19	0.26
ns			0.42		
cc	0.11	0.02		0.09	0.07
H_2O	0.47	0.31	0.32	0.18	0.12
Rest	0.11	0.22	0.14	0.14	0.12
Total	100.49	100.48	100.07	99.75	99.98
Qz	11.3	24.0	24.3	23.6	23.6
or	30.4	29.1	33.6	32.4	33.7
ab	58.3	46.9	42.1	44.0	42.7
or	34.2	38.3	44.4	42.5	44.1
ab	65.8	61.7	55.6	57.5	55.9
an	0.0	0.0	0.0	0.0	0.0
$\frac{100 \times FeO}{FeO + MgO}$ molec. in femics	0.0	73.7	41.7	0.0	0.0

TABLE 35

CHEMICAL ANALYSES OF NANDEWAR ANDESITES AND TESCHENITE

(all analyses by M.J. Abbott)

	CTS	151-3A	151-3
SiO_2	45.20	55.47	56.23
TiO_2	2.42	1.14	1.12
Al_2O_3	13.39	17.76	17.71
Fe_2O_3	2.97	4.75	3.49
FeO	8.81	3.03	3.10
MnO	0.19	0.10	0.11
MgO	10.20	4.86	3.63
CaO	10.12	7.45	7.84
Na_2O	2.51	3.63	3.47
K_2O	1.80	1.24	1.15
P_2O_5	0.73	0.40	0.43
H_2O^+	1.60	0.40	0.88
H_2O^-	.	.	.
CO_2	0.01	0.01	0.03
Rb_2O	tr	tr	tr
SrO	0.10	0.08	0.09
ZrO_2	0.03	0.02	0.02
BaO	0.05	0.07	0.07
Total	100.13	100.41	99.37
Kuno S.I.	38.80	27.76	24.46
Larsen Index	-12.27	+4.39	+5.32

$$\text{Kuno S.I.} = \frac{MgO \times 100}{MgO + FeO + Fe_2O_3 + Na_2O + K_2O}$$

$$\text{Larsen Index} = 1/3\ SiO_2 + K_2O - FeO - MgO - CaO$$

Localities and rock type of specimens listed in Table 28 .

TABLE 36

C.I.P.W. NORMS OF NANDEWAR ANDESITES AND TESCHENITE, FROM ANALYSES LISTED IN TABLE 35. (SAME NUMBERS HAVE BEEN USED).

Localities and rock type of specimens listed in Table 28.

		CTS	151-3A	151-3
Qz			8.80	11.61
or		10.64	7.33	6.80
ab		14.60	30.72	29.36
an		19.95	28.51	29.35
ne		3.59		
wo	di	10.61	2.41	2.73
en	di	7.05	2.09	2.15
fs	di	2.80		0.28
en	hy		10.02	6.89
fs	hy			0.89
fo	ol	12.86		
fa	ol	5.63		
il		4.60	2.17	2.13
mt		4.31	6.79	5.06
ap		1.73	0.95	1.02
cc		0.02	0.02	0.07
H_2O		1.60	0.40	0.88
Rest		0.18	0.17	0.18
Total		100.17	100.38	99.40
or		23.5	11.0	10.4
ab		32.3	46.2	44.8
an		44.2	42.8	44.8
$\frac{100 \times FeO}{FeO + MgO}$ molec. in femics.		23.1	0.0	8.9

a relatively iron-rich composition (the modal olivine has a composition of Fa_{26}).

It will be noted in the table set out below that in the basalts E7, 5P, Gr 1 and E8 the $\frac{Fe^{2+}}{Fe^{2+} + Mg}$ ratio in the modal olivines is much greater than the corresponding ratio in the normative ferromagnesian minerals.

Rock	$\frac{Fe^{2+} \times 100}{Fe^{2+} + Mg}$ molecular ratio	
	Normative	Modal
E7	19.4	31.0
5P	11.8	23.0
Gr 1	16.7	26.0
E8	23.9	34.0

It is assumed that oxidation of the rocks (which will give higher normative mt, and hy, and lower ne, if present, and fs and fa) is responsible for the discrepancies in the ratios in the table above. If the iron is calculated into normative mt, extra silica is available, and this goes into normative hy, and this will account for some of the normative hy in alkali-olivine basalts (Coombs, 1963). An analysis of the porphyritic olivine basalt 5P (some of the oxide values have been subsequently amended in this analysis, so it is labelled 5P'), and the norm calculated from it, together with a norm calculated with the $Fe^{2+}/Fe^{2+} + Mg$ ratio adjusted to that of the modal olivine (5P") are set out in Table 37 . The normative hy is lower if the $Fe^{2+}/Fe^{2+} + Mg$ ratio is adjusted to that of the modal olivine, the ol is higher, and the mt is, of course, lower. Despite a change in the ferromagnesian ratio from 11.1 (normative) to 23.0 (modal), and the accompanying changes in the norm, there is still some hy and no

TABLE 37

NORM CALCULATIONS FOR THE OLIVINE BASALT 5P.

	5P'	5P"
SiO_2	48.17	48.17
TiO_2	2.39	2.39
Al_2O_3	17.67	17.67
Fe_2O_3	4.11	2.28
FeO	5.09	6.00
MnO	0.09	0.09
MgO	5.31	5.31
CaO	9.70	9.70
Na_2O	3.26	3.26
K_2O	1.68	1.68
P_2O_5	0.64	0.64
Total	98.11	97.19

NORMS		5P'	5P"
or		9.93	9.93
ab		27.58	27.58
an		28.62	28.62
di	di	10.60	9.18
he	di	1.52	3.14
en	hy	2.96	0.80
fs	hy	0.48	0.31
fo	ol	3.74	5.72
fa	ol	0.67	2.47
mt		5.96	3.31
il		4.54	4.54
ap		1.51	1.51
Total		98.11	97.11
Molec. $\frac{Fe^{2+}}{Fe^{2+} + Mg}$ in femics		11.1	23.0

5P' analysis of olivine basalt (this analysis has subsequently had some oxide values amended, see 5P, Table 29).

5P" recalculated analysis and norm to convert the molecular $Fe^{2+}/Fe^{2+} + Mg$ ratio of the ferromagnesian minerals in the norm from the value 11.1 to 23.0, the value for the modal olivine.

ne. A similar situation is presumed to exist for all the other olivine basalts, and they are all thus saturated in silica. Yoder and Tilley (1962) note that oxidation relations increase the Q + hy in the norm, although if these normative components are already present, the ultimate course of differentiation will not be altered. The trachyandesite glass BG has quartz and hematite in the norm because of the high state of oxidation of this rock.

The SiO_2 values for the series have been plotted against the Kuno S.I. in Fig. 10 . The SiO_2 is relatively constant in values in the basalts and trachyandesites, but rises sharply in the two felspar trachytes to the comendites. This trend has been noted for other alkaline series with this type of graph (e.g. Saggerson and Williams, 1964), but the trend contrasts remarkably with that from strongly undersaturated rocks (op. cit., Fig. 13). The two Permian calc-alkaline andesites from the Nandewars plot well above the curve for the alkaline series (Fig. 10) and this suggests that on a Kuno S.I. diagram, the calc-alkaline silica variation against S.I. would be a straight line. The Kuno S.I. plotted against silica shows the change in silica content of a rock series moving along a differentiation trend in the familiar FMA triangle.

The Kuno S.I. has one defect, however, of being constructed mainly from one variable, MgO. The points on the diagram tend to be crowded into the low S.I. region where the MgO is low, particularly for alkaline series. In the Nandewar series many extreme differentiates exist in which the MgO is very low, and the points for these rocks are concentrated into the low S.I. end of the diagram (Fig. 10). The Larsen (1938) index ($1/3\ SiO_2 + K_2O - FeO - MgO - CaO$) is calculated from more variables, and gives a better spread of plotted points with both petrographic and chemical types.

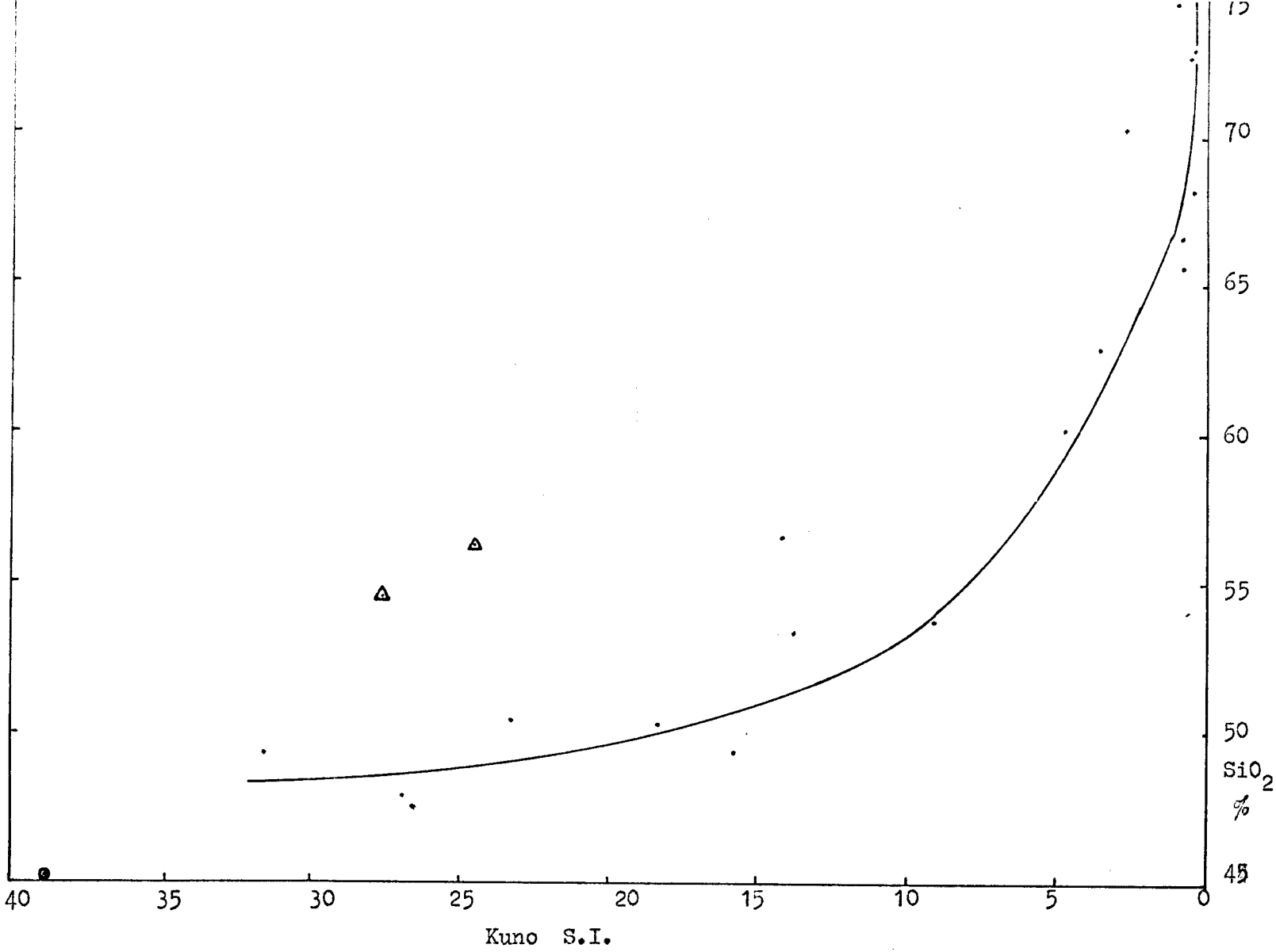

Figure 10

Plot of silica against Kuno solidification index (see text). In this and the following figures, the calc-alkaline andesites are shown in triangles, and the contact teschenite is shown by a circled dot. The other Nandewar rocks are shown by dots.

The use of Harker diagrams for volcanic rocks, particularly in basalt-trachyte sequences, is not advisable (Chayes, 1964b). All the oxides (except P_2O_5 and MnO) have been plotted against the Larsen index.

The SiO_2, plotted against the Larsen Index (Fig. 11), rises steadily throughout the series, the rate of increase itself increasing in the late differentiates, where the silica reaches quite high values (73.82 per cent maximum).

No trend could be deduced from the plot of alumina against the Larsen index (Fig. 12), although the comendites 104-E, Mt L, Mt W and the trachytes 100-6 and GOV4 have lower alumina, from 13 per cent to 15 per cent. The alumina content of the contact teschenite is lower than that of the olivine basalts of the saturated alkaline series.

The TiO_2 (Fig. 12) decreases steadily with differentiation in the alkaline rocks, but the values for the Permian calc-alkaline andesites are much lower than the trend for the alkaline rocks.

The total iron (recalculated as Fe_2O_3) plotted in Fig. 13 , decreases steadily in the basalts and trachyandesites, and this fall becomes more rapid in the trachytes and comendites. FeO (Fig. 14) decreases throughout, and the comendites 73-5, 73-12, and 104-E are extremely depleted in FeO. The FeO values of the calc-alkaline andesites are lower than those in the alkaline series at equivalent stages of differentiation. Fe_2O_3 (Fig. 14) rises at first in differentiation from the basalts to trachyandesites, and then falls gradually in the trachytes and comendites.

The MgO (Fig. 15) and CaO (Fig. 15) decrease steadily in the series. The contact teschenite has much higher values for both these oxides than the alkaline saturated series.

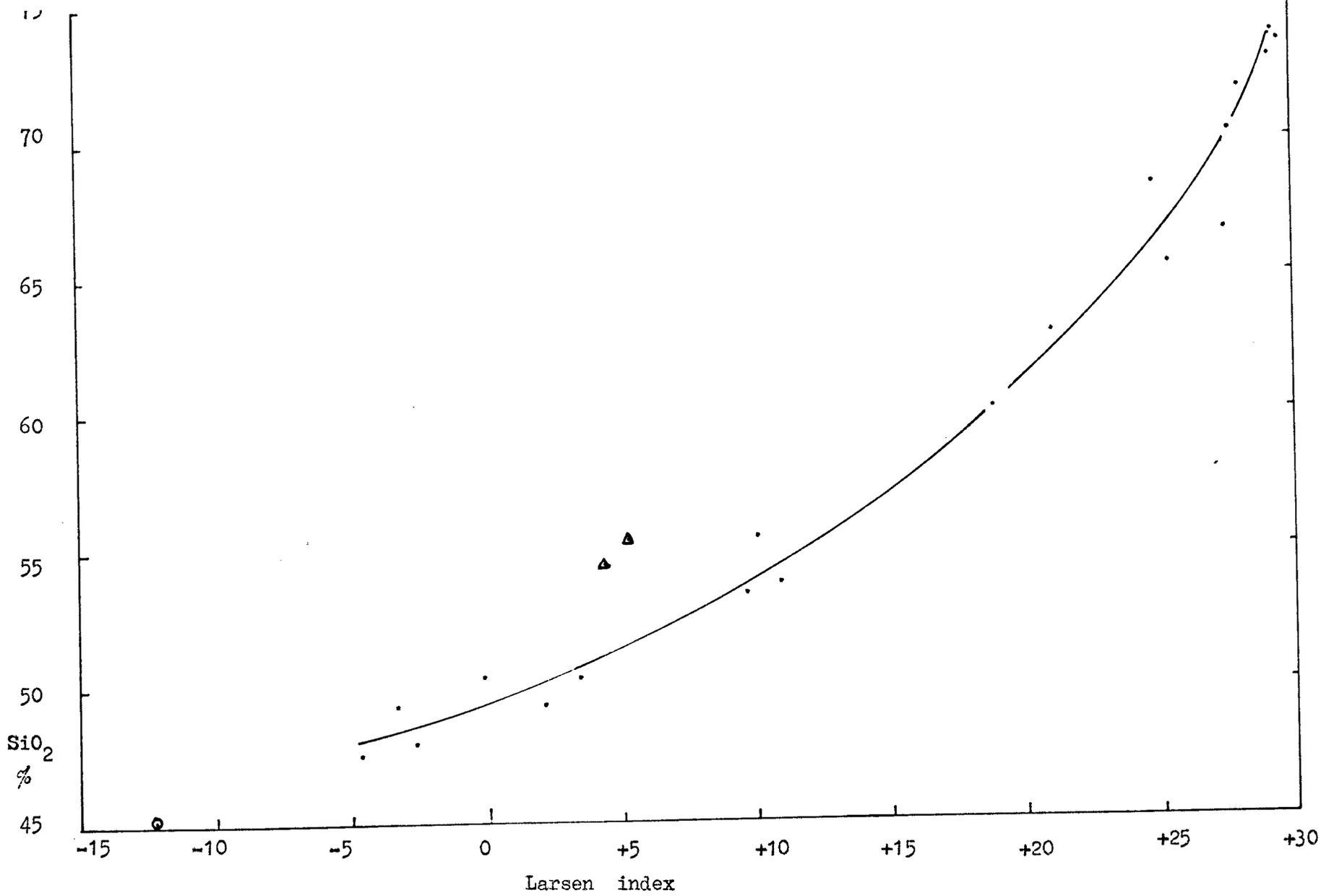

Figure 11

Plot of silica against Larsen index ($1/3\ SiO_2 + K_2O - FeO - MgO - CaO$).

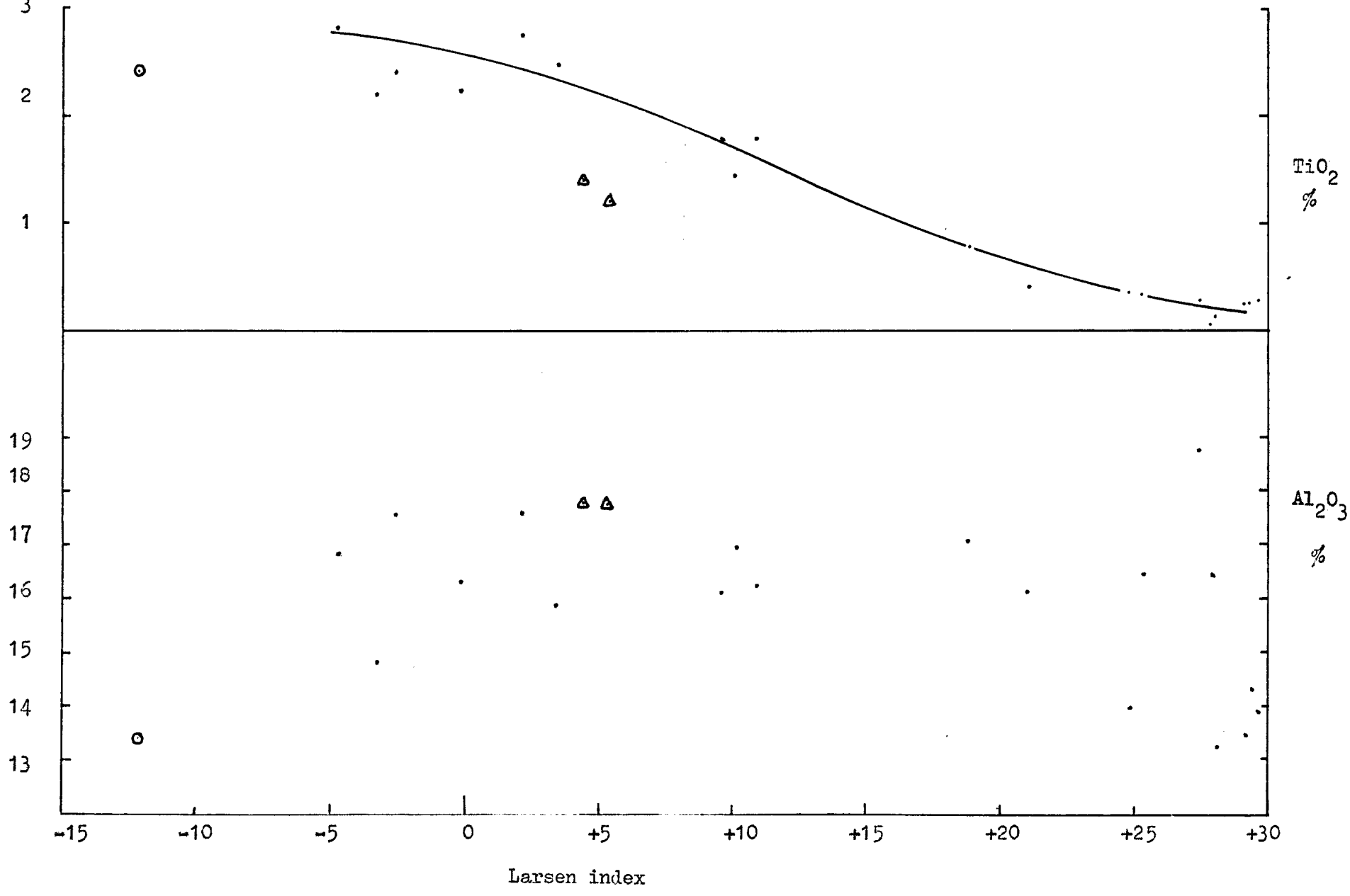
3
2
1
TiO_2
%
19
18
17
16
15
14
13
Al_2O_3
%
-15
-10
-5
0
+5
+10
+15
+20
+25
+30
Larsen index

Figure 12

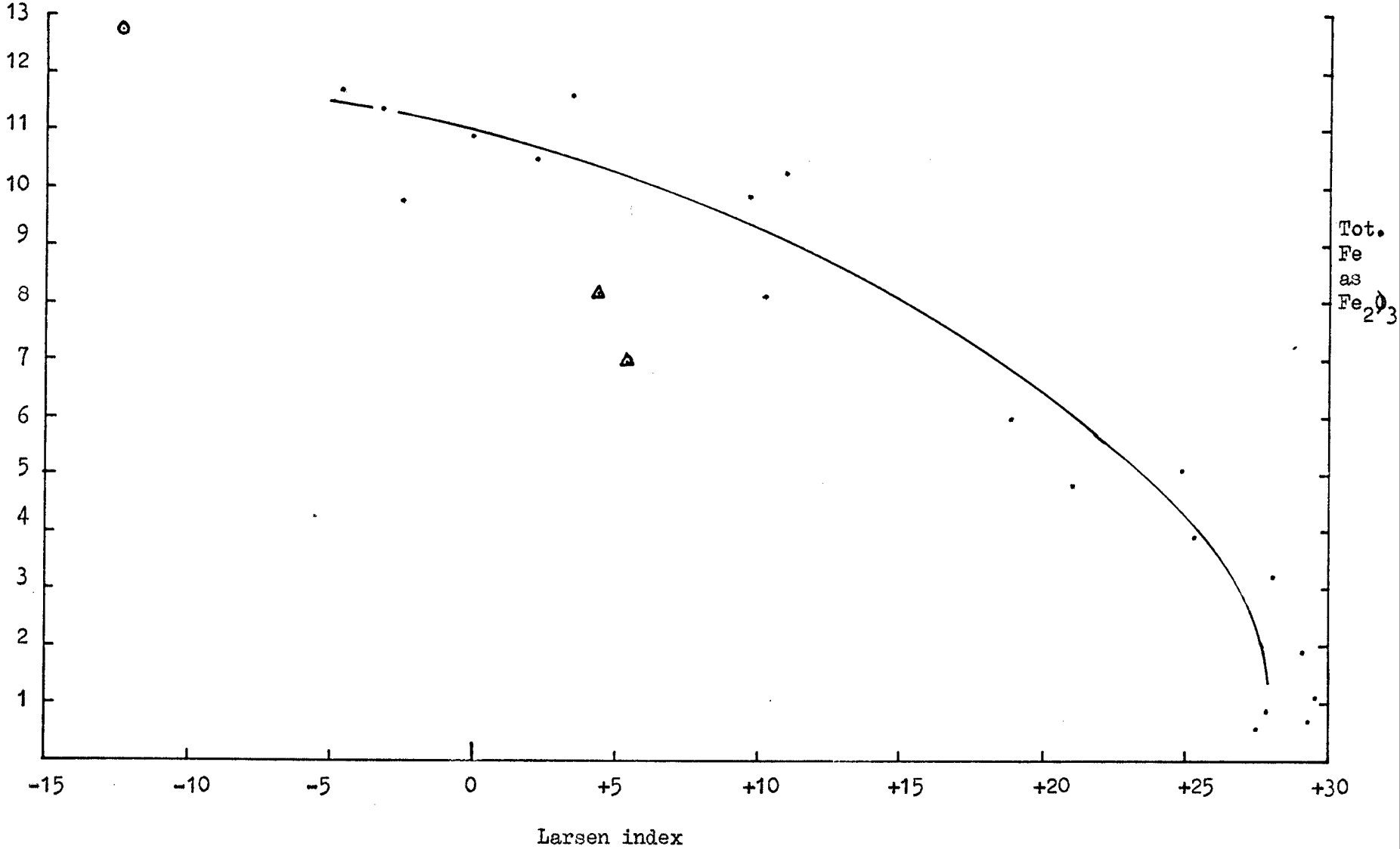
13
12
11
10
9
8
7
6
5
4
3
2
1
Tot. Fe as Fe_2O_3
-15
-10
-5
0
+5
+10
+15
+20
+25
+30
Larsen index

Figure 13

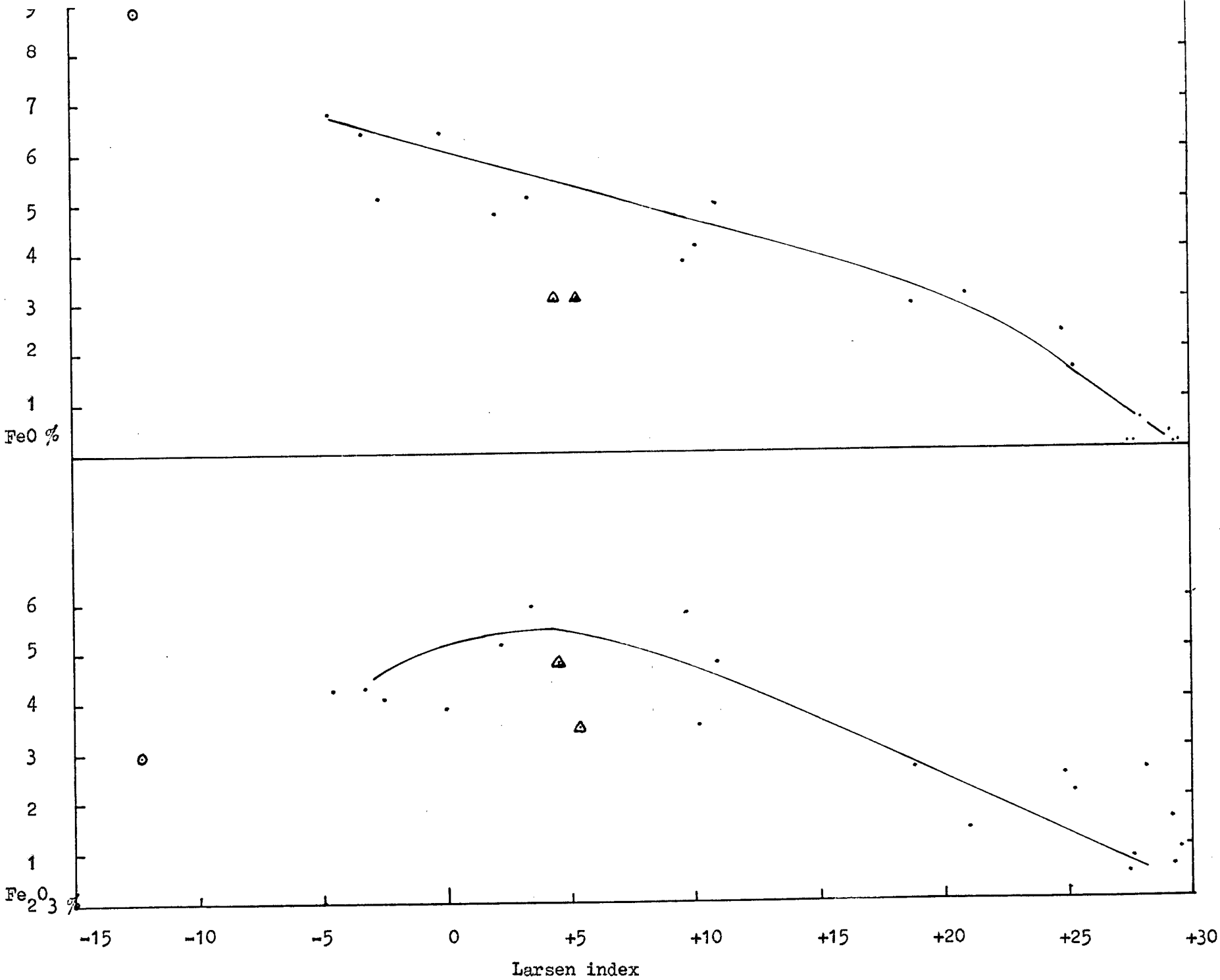
9
8
7
6
5
4
3
2
1
FeO %
6
5
4
3
2
1
Fe_2O_3 %
-15
-10
-5
0
+5
+10
+15
+20
+25
+30
Larsen index

Figure 14

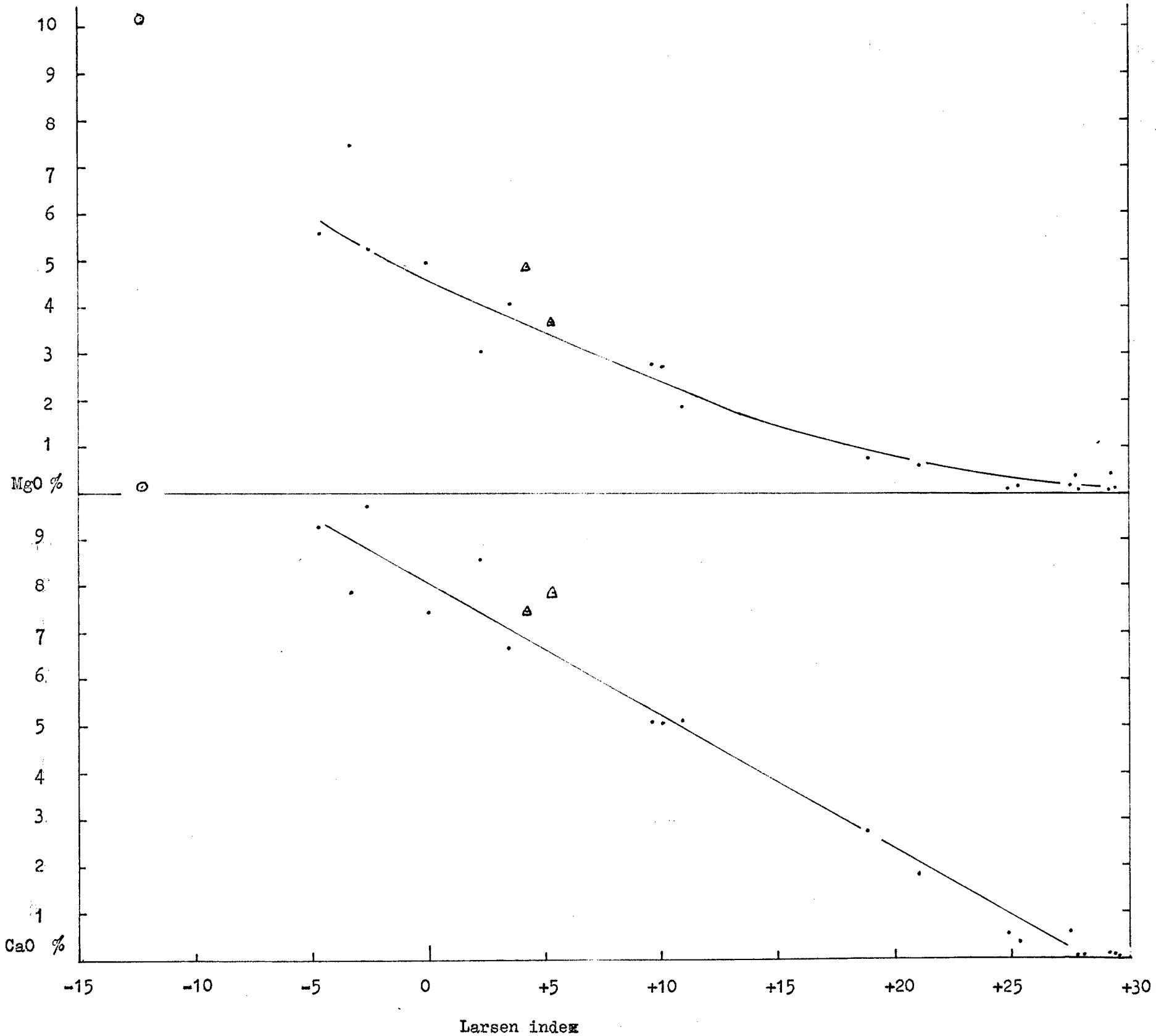
10
9
8
7
6
5
4
3
2
1
MgO %
9
8
7
6
5
4
3
2
1
CaO %
-15
-10
-5
0
+5
+10
+15
+20
+25
+30
Larsen index

Figure 15

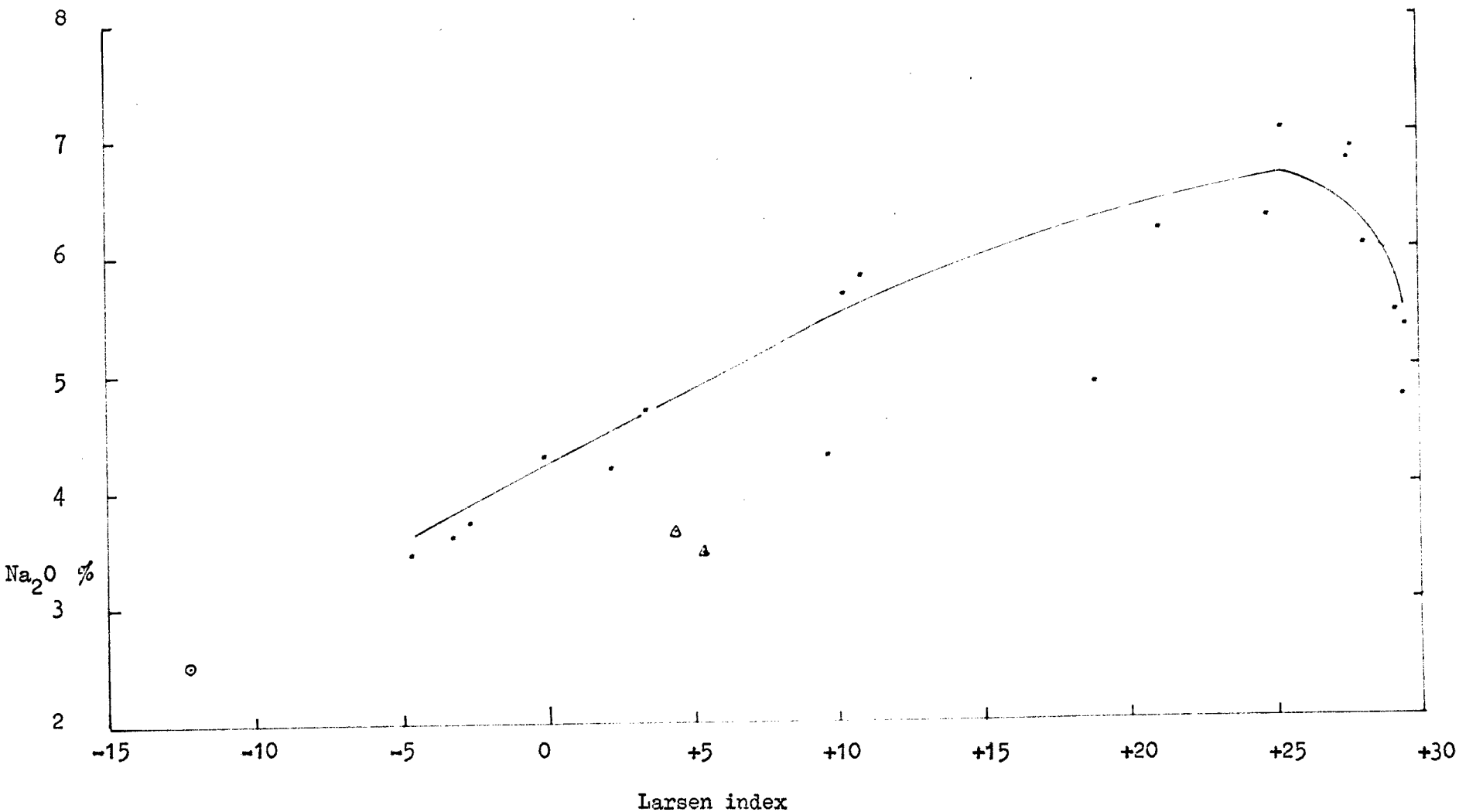

Figure 16

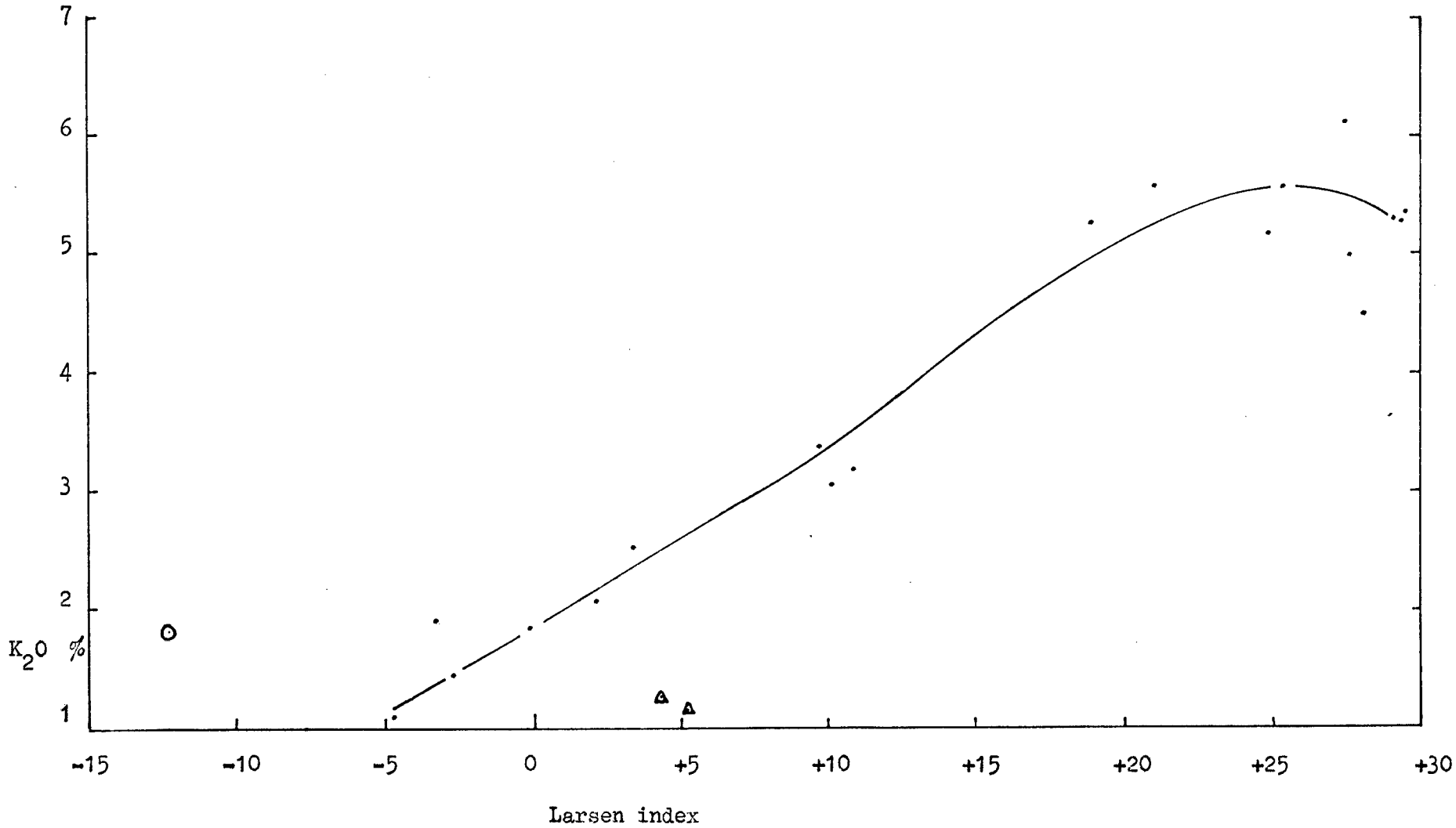

Figure 17

The Na_2O (Fig. 16) increases from the basalts through the trachyandesites to the trachytes, and reaches a maximum in one of the cossyrite trachytes. It then falls rapidly in the trachytes 100-6 and Mt W and the comendites Mt L and 104-E, and this fall is due to the fact that the felspar has reached the minimum melting composition of $Ab_{65}Or_{35}$, and subsequent differentiation will only add quartz, increasing the quartz/felspar ratio. All the trachytes and comendites with low Na_2O have more than 20 per cent normative quartz.

The K_2O (Fig. 17) shows a similar trend to the sodium, although it rises in value more rapidly, but does not decrease as markedly in the final differentiates. The calc-alkaline andesites have both lower Na_2O and K_2O than the alkaline series.

All the oxide values for the contact teschenite plot off the basic end of the saturated alkaline trend.

The oxides MgO, FeO + Fe_2O_3, Na_2O + K_2O have been plotted on the FMA triangle (Fig. 18). The alkaline series shows little absolute iron enrichment from olivine basalts to trachyandesites. The relatively differentiated nature of the olivine basalts can be seen by the fact that the points plot comparatively close to the iron - alkalies sideline, revealing impoverishment in Mg in comparison to the trends figured by Le Maitre (1962, Fig. 11) for various Atlantic Ocean alkaline provinces, and to the Hawaiian trends from Macdonald and Katsura (1964), and the trends of various alkaline series plotted by Nockolds and Allen (1954).

After this initial moderate iron enrichment, the dominant trend exhibited by the Nandewar series is very extreme alkali enrichment which occurs mainly at the expense of the total iron, since nearly all the MgO

normative compositions in the Q - or - ab system compared to the felspar compositions on the or - ab sideline. The preferential enrichment in potash is only very small, and not as extreme as proposed by Carmichael (1962) for the strongly peralkaline pantellerites.

The main normative trends shown by the alkaline series can be summarised as follows: increase in or up to a limiting value of about 31-32 per cent (when the felspar reaches the minimum melting composition); increase of ab up until the trachyte stage of differentiation, and then a fall as the amount of normative quartz rises; a steady decrease of an, which of course disappears entirely in the peralkaline rocks; a decrease of di, hy, and ol, the ol disappearing from the trachytes altogether as normative quartz appears; and a decrease of mt, il, and ap. As noted before, the normative component ns appears in only two of the peralkaline trachytes (GOV4 and Mt W).

In the two felspar trachyte KG and the comendites 73-5 and 104-E normative corundum (C) appears. In the trachyte KG much of the CaO has been combined with the large amount of CO_2 to form calcite (cc), and the Al_2O_3 not used to form an calculates as C. It is unlikely that the modal carbonate, quite common in this rock, is entirely calcite, but it is probably sideritic, since it pseudomorphs olivine of composition of Fa_{40}. Wilkinson (1958) records carbonate close to siderite in composition (70-80 per cent $FeCO_3$) in gabbro teschenites, although this is regarded as a late stage (presumably deuteric) mineral. If the carbonate from KG is sideritic, then CaO will be released and calculated as normative an and normative C will disappear. The amounts of normative C in the comendites 73-5 and

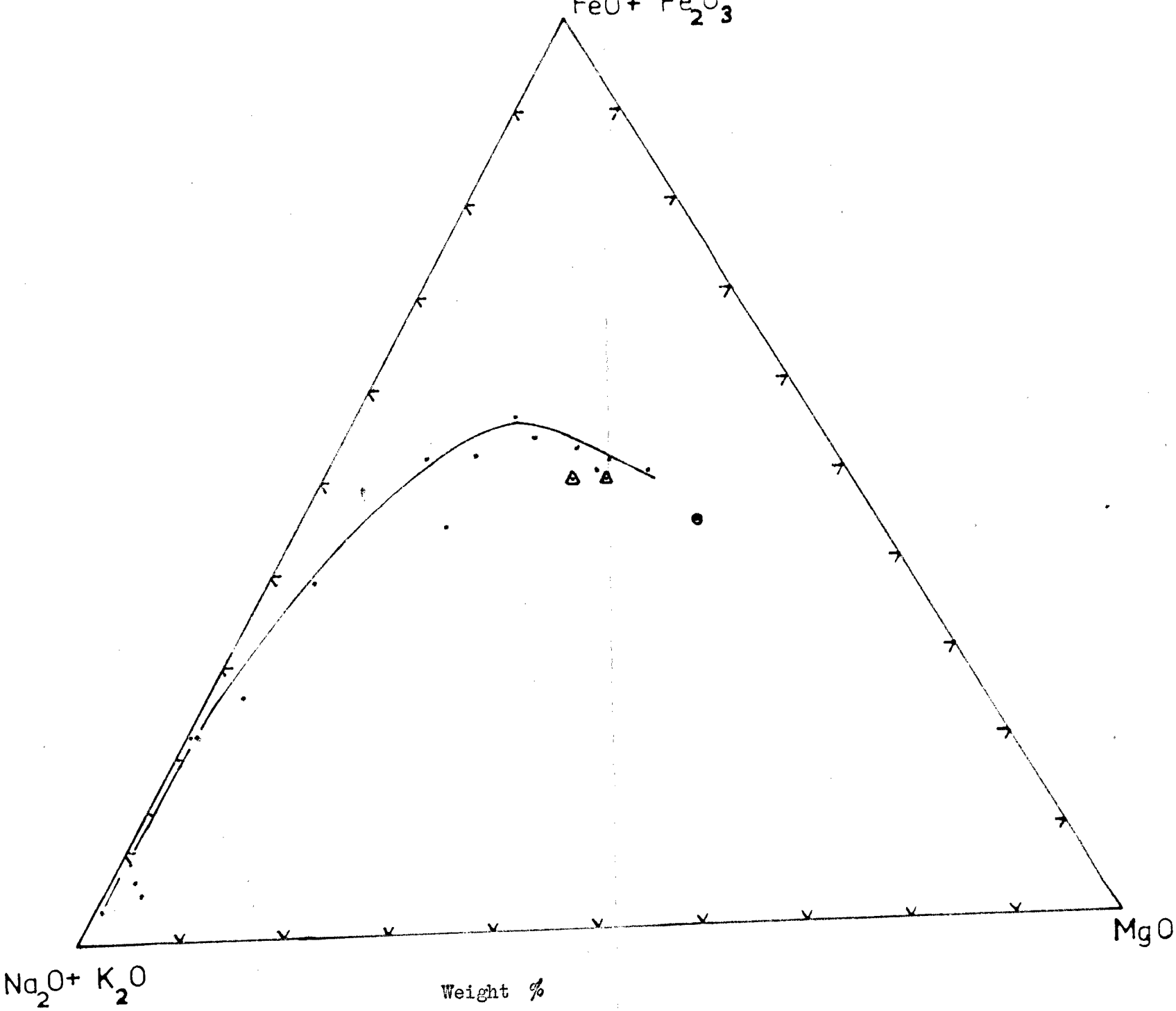

Figure 18

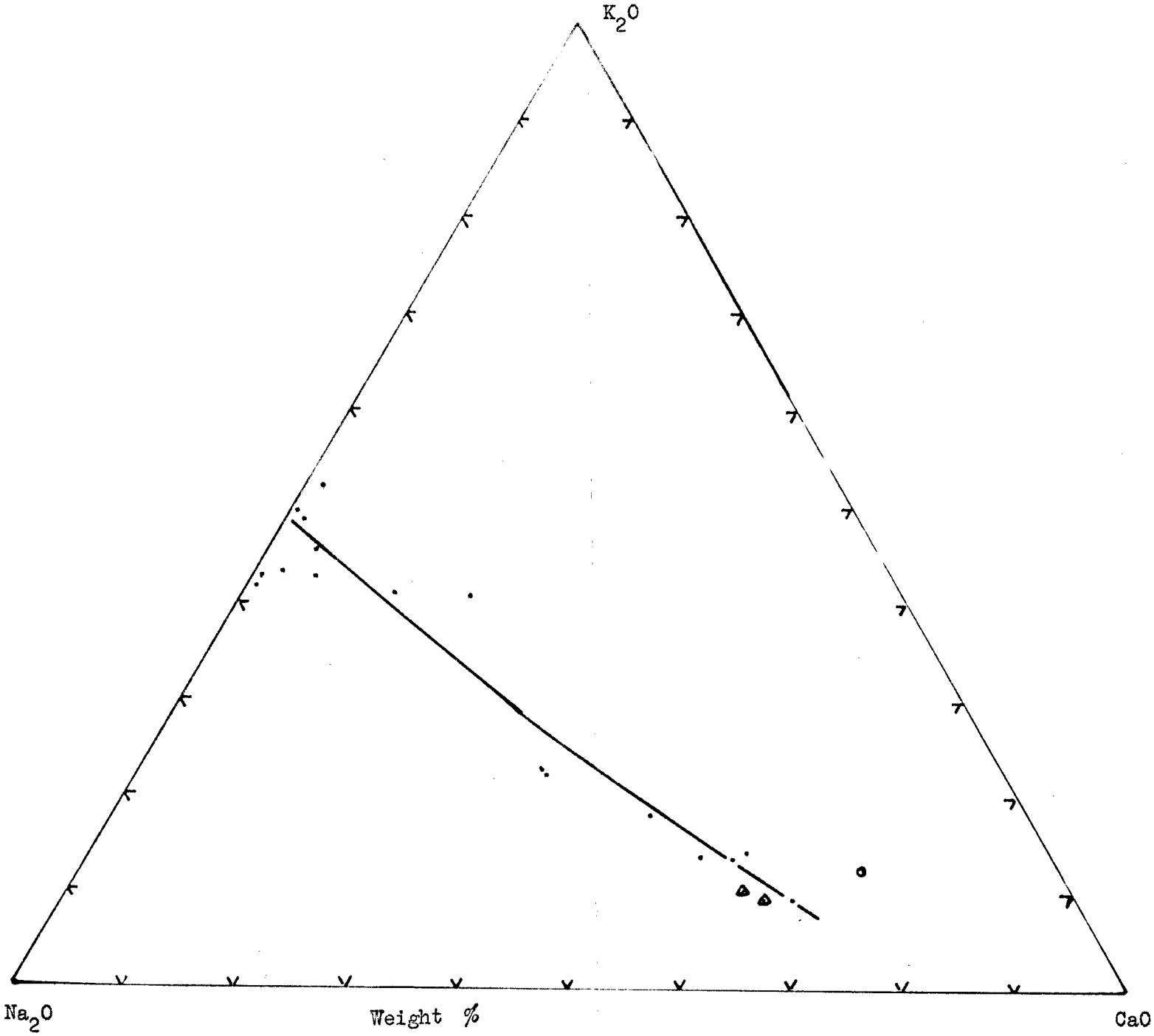

Figure 19

is removed after the trachyandesite stage of differentiation. The final differentiates (73-5, 73-12, 104-E and Mt L) approach very closely to the alkalies apex of the FMA triangle. This extreme enrichment in alkalies is unusual and is not seen in any of the alkaline series figured by Le Maitre (1962, Fig. 11) or in the Hawaiian alkaline series (Macdonald and Katsura, 1964). The Nandewar final differentiates possess only quartz and alkali felspar, with no ferromagnesian minerals at all.

The rocks in the alkaline series become peralkaline (molecular ratio $\frac{Na_2O + K_2O}{Al_2O_3}$ greater than 1) when the cossyrite trachyte stage of differentiation is reached, and these trachytes have peralkalinity ratios from 1.10 to 1.15. This contrasts with the comendites, which are either just peraluminous or peralkaline (ratios range from 0.95 to 1.05). The peralkalinity of the trachytes is not as extreme as in the pantellerites from Pantelleria, some of which have an excess of soda alone over alumina (Carmichael, 1962; Chayes, 1962) although the alkalies are higher in the Nandewar trachytes; the high peralkalinity of the pantellerites is due to the very low Al_2O_3. Chemically, the Nandewar peralkaline trachytes (Mt W and 100-6 in particular) are closer in composition to the comendites ('Commende' type, Chayes, 1962). Although the normative ac appears in all the peralkaline trachytes, ns appears in only two of them (GOV4, ns = 0.44 and Mt W, ns = 0.42).

The analyses have been plotted in the CaO - K_2O - Na_2O triangle (Fig. 19); the trend with increasing differentiation proceeds away from the CaO apex towards the Na_2O - K_2O sideline. There is only very slight preferential enrichment in potash over soda with differentiation. This feature has also been noted (see section Felspars) from a study of the bulk

104-E are small enough to perhaps be accounted for by slight errors in the determination of the alkalies and CaO, which will affect the amount of normative felspar formed, and hence the amount of Al_2O_3 used.

The Fe^{2+}/Fe^{2+} + Mg x 100 molecular ratios in the ferromagnesian minerals in the norm have been tabulated (Tables 30 , 32 , and 34). The ratio increases with differentiation from the basalts and trachyandesites to the peralkaline cossyrite trachytes, in which the ratio has a maximum value of about 95; thus showing the relative Fe^{2+} enrichment over Mg. There are exceptions to this trend. In the basalts the reason for the normative molecular Fe^{2+}/Fe^{2+} + Mg ratios being lower than the modal values from the olivines has been ascribed to oxidation of the rock. The difference between the ferromagnesian Fe^{2+}/Fe^{2+} + Mg ratios of the norm and those of the olivines in the olivine basalts has already been considered. In the trachyandesite 10 the Fe^{2+}/Fe^{2+} + Mg x 100 ratio in the analysed clinopyroxene (29.8) is much higher than that of the norm (2.2), and as noted before, recalculation of the norm to the Fe^{2+}/Fe^{2+} + Mg ratio of the clinopyroxene will decrease the normative Qtz and hy, and increase the ol.

The trachyandesite glass BG is so oxidised that normative hm appears, and the Fe^{2+}/Fe^{2+} + Mg molecular ratio in the normative ferromagnesian minerals is zero.

The Fe^{2+}/Fe^{2+} + Mg x 100 ratios in the normative ferromagnesian minerals in the cossyrite trachytes are high and range from 74 to 95, although the trachyte Mt W has a ratio of 42. These high ferromagnesian ratios are due to the presence of hedenbergites, arfvedsonites and cossyrites, all mineral phases with very little MgO, and also to the fact that the ferrous iron enters the normative di and hy rather than combining with Fe^{3+} in

magnetite, since the Fe^{3+} combines with the Na to form acmite. The comendites 73-5, 73-12, Mt L and 104-E by contrast, have molecular Fe^{2+}/Fe^{2+} + Mg ratios in the normative ferromagnesian minerals of zero, since the oxidation ratio is high, the Fe^{3+} being high enough to form normative hm, as well as using all the Fe^{2+} to form magnetite. Furthermore, the total iron, in particular the Fe^{2+}, is much lower in the comendites than in the cossyrite trachytes.

There are thus contrasts between the cossyrite trachytes and the comendites: the former are peralkaline while the latter are either just peraluminous or just peralkaline; and the cossyrite trachytes have higher Fe^{2+}/Fe^{2+} + Mg ratios in the normative ferromagnesian minerals as well as higher total iron (particularly FeO) and higher total rock $\frac{FeO + Fe_2O_3 + MnO}{FeO + Fe_2O_3 + MnO + MgO}$ ratios and lower oxidation ratios $\frac{Fe_2O_3}{Fe_2O_3 + FeO}$ than the comendites. The relevant data are set out below:

	Cossyrite trachytes			Comendites			
	24	GOV4	Mt W	73-5	73-12	Mt L	104-E
Total rock $\frac{FeO + Fe_2O_3}{FeO + Fe_2O_3 + MgO}$	96.4	98.6	96.8	82.5	70.7	88.9	59.8
Total Rock $\frac{Fe_2O_3}{FeO + Fe_2O_3}$	56.6	51.4	84.3	78.9	89.7	91.5	89.5
Normative ferromag. Fe^{2+}/Fe^{2+} + Mg x 100	82.5	94.5	41.7	0.0	0.0	0.0	0.0
Peralkalinity ratio $\frac{Na_2O + K_2O}{Al_2O_3}$ (molecular)	1.07	1.14	1.10	0.95	1.01	1.04	0.95

The analysed rocks from the Nandewar alkaline series do not furnish any examples of peralkaline trachytes with high oxidation ratios; the comendites with high oxidation ratios $\frac{Fe_2O_3}{Fe_2O_3 + FeO}$ are close to having a 1:1 molecular ratio of $Na_2O + K_2O$: Al_2O_3. Since the comendites are simply mixtures of quartz and alkali felspars the ratio should be exactly 1, and from the analyses of felspars (Deer, Howie and Zussman, 1963, vol. 4) nearly all the iron should be ferric (this has been assumed in the felspar analyses in this thesis).

The final differentiates (the comendites) trend towards the minimum melting composition in the system Q - or - ab, Fig. 9 , (Tuttle and Bowen, 1958), and the comendites have from 91.3 to 97.4 per cent of Q + ab + or components in the norm. This is very strong evidence of fractional crystallisation of these rocks, and further evidence comes from a study of the felspars (see the section on Felspars).

TRACE ELEMENTS

The trace elements Zr, Sr, Ba, and Rb have been determined by X-ray fluorescent spectography, and the elements U, Th, and K have been determined by γ-rays by Dr. K.S. Heier.

Values are available for Zr, Sr, Ba, and Rb for all the analysed rocks including all the alkaline rocks ranging from olivine basalts to comendites, a chilled contact teschenite, and two Permian calc-alkaline andesites. The U and Th values are available for some selected rocks from the alkaline series (including the contact teschenite). Zr, Sr, Ba, and Rb values are set out in Table 38 ; the U, Th, and K values (γ-ray) together with Th/U, Th/K x 10^4, and U/K x 10^4 ratios are set out in Table 39 ; Ba/Rb, Ba/Sr, Ba/K x 10^3, and Sr/Ca x 10^3 ratios and felsic index $\frac{(Na + K) \times 100}{Na + K + Ca}$ for each of the rocks are set out in Tables 40-41; and the Th/Zr x 100 ratios are set out in Tables 40-41.

Rubidium:

The Rubidium contents of the basic rocks from the Nandewars including the chilled contact teschenite and olivine basalts are low and range from 20 to 40 ppm. The values for the trachyandesites range up to 60 ppm, and the Rb rises in the trachytes and comendites, ranging from 100 to 250 ppm in these latter rocks. The Rb of the Permian andesites is low at about 20 ppm.

The series of alkaline rocks studied geochemically by Nockolds and Allen (1954) show basically similar ranges for Rb. The Hawaiian rocks (op. cit. Table 11) possess a somewhat higher Rb throughout, the Scottish Tertiary basalt -- trachyte series (op. cit. Table 10) possesses

TABLE 38

TRACE ELEMENTS IN NANDEWAR ROCKS, ALL EXPRESSED IN PARTS PER MILLION BY WEIGHT.

(all analyses by M.J. Abbott, by X-ray fluorescent spectrography).

Element	Ionic radius Å	E7	5P	Gr1	10	15	E8	BG	8A	118-2
Zr^{4+}	0.79	127	190	218	221	327	208	398	393	345
Sr^{2+}	1.12	813	897	581	856	742	736	627	645	536
Ba^{2+}	1.34	868	533	674	666	835	2735	1433	1324	1487
Rb^{+}	1.47	19	30	41	38	50	33	68	60	64

Element	KG	151-2	24	GOV4	73-5	73-12	100-6	MtW	MtL	104-E
Zr^{4+}	345	936	668	722	835	622	1405	811	903	715
Sr^{2+}	313	82	1	1	15	2	1	5	1	6
Ba^{2+}	1479	476	4	8	312	4	12	50	8	28
Rb^{+}	71	107	116	139	150	257	281	259	185	160

Element	CTS	151-3A	151-3
Zr^{4+}	206	166	154
Sr^{2+}	847	687	775
Ba^{2+}	421	657	642
Rb^{+}	27	20	22

Localities and rock type of specimens listed in Table 28 .

TABLE 39

URANIUM AND THORIUM VALUES FOR NANDEWAR ROCKS, ANALYST K.S. HEIER.
ALL VALUES EXPRESSED IN PARTS PER MILLION BY WEIGHT.

	CTS	E7	5P	Gr1	10	15	BG	8A
U	1.1	0.70	0.88	1.0	0.70	1.5	1.7	1.3
Th	3.8	2.2	3.3	4.2	4.3	5.8	5.7	4.9
Th/U	3.5	3.1	3.8	4.2	8.6	3.9	3.4	3.8
Th/K x 10^4	2.6	2.5	2.7	2.7	2.9	2.8	2.1	2.9
U/K x 10^4	0.74	0.79	0.73	0.63	0.34	0.72	0.61	0.76
K per cent	1.49	0.89	1.21	1.58	1.46	2.09	2.78	1.70

	KG	151-2	24	GOV4	73-5 73-12	100-6	Mt W	Mt L	104-E
U	1.8	6.2	2.8	0.87	2.8	3.3	3.3	5.2	4.1
Th	7.0	29.1	13.0	16.8	24.6	41.8	19.2	21.4	17.9
Th/U	3.9	4.7	4.6	19	8.8	12.7	5.8	4.1	4.2
Th/K x 10^4	1.6	7.9	2.8	3.8	5.4	11.0	4.3	4.8	3.8
U/K x 10^4	0.41	1.7	0.60	0.20	0.61	0.87	0.74	1.2	0.91
K per cent	4.43	4.69	4.69	4.42	4.57	3.80	4.44	4.42	4.55

Index of specimens and rock types in Table 28 . 73-5 and 73-12 is a composite sample, consisting of about equal proportions of each comendite. The K values are those of Heier, derived, together with the U and Th values, by gamma ray spectrography.

TABLE 40

TRACE ELEMENT RATIOS CALCULATED FROM DATA IN TABLES 38 and 39. SPECIMEN NUMBERS, ROCK TYPES, AND LOCALITIES AS IN TABLE 28.

	CTS	E7	5P	Grl	10	15	E8	BG
Ba/Rb	15.6	45.7	17.8	16.4	17.5	16.7	82.9	21.1
Ba/Sr	0.5	1.1	0.6	1.2	0.8	1.1	3.7	2.3
$\frac{Ba \times 10^3}{K}$	28.3	96.4	44.8	42.7	38.9	40.1	178.8	51.4
$\frac{Sr \times 10^3}{Ca}$	11.7	12.3	12.9	10.4	14.0	15.6	13.9	17.2
Felsic index $\frac{(Na + K) \times 100}{Na + K + Ca}$	31.7	34.4	36.4	43.2	43.9	53.8	46.9	62.0
$\frac{Th \times 10^2}{Zr}$	1.84	1.73	1.74	1.93	1.95	1.77		1.43
K/Rb	532	474	397	385	450	416	464	410

	8A	151-3A	151-3	118-2	KG	151-2	24
Ba/Rb	22.1	32.9	29.2	23.2	20.8	4.5	0.03
Ba/Sr	2.1	1.0	0.8	2.8	4.7	5.8	4.0
$\frac{Ba \times 10^3}{K}$	50.0	63.8	67.6	58.3	33.8	103.0	0.87
$\frac{Sr \times 10^3}{Ca}$	17.5	12.9	13.8	14.8	15.9	6.3	0.04
Felsic index $\frac{(Na + K) \times 100}{Na + K + Ca}$	65.3	41.2	38.6	65.1	80.2	87.5	97.4
$\frac{Th \times 10^2}{Zr}$	1.25				2.03	3.11	1.95
K/Rb	442	515	432	398	615	432	398

TABLE 41

TRACE ELEMENT RATIOS CALCULATED FROM DATA IN TABLES 38 and 39 .
SPECIMEN NUMBERS, ROCK TYPES, AND LOCALITIES AS IN TABLE 28 .

	GOV4	73-5	73-12	100-6	Mt W	Mt L	104-E
Ba/Rb	0.06	2.08	0.02	0.04	0.19	0.04	0.18
Ba/Sr	8.0	20.8	2.0	12.0	10.0	8.0	4.67
$\frac{Ba \times 10^3}{K}$	1.9	61.5	1.0	3.2	1.1	1.8	6.3
$\frac{Sr \times 10^3}{Ca}$	0.02	0.34	0.33	0.16	0.42	0.33	0.75
Felsic index $\frac{(Na + K) \times 100}{Na + K + Ca}$	94.8	95.8	99.4	99.3	98.6	99.6	99.0
$\frac{Th \times 10^2}{Zr}$	2.33	3.37		2.98	2.37	2.37	2.50
K/Rb	309	338	161	133	171	236	278

lower Rb values, while the undersaturated Polynesian basalt -- phonolite series has much higher Rb throughout. Wager and Mitchell (1953) have also studied the geochemistry of the Hawaiian alkaline series, and their Rb values agree with those of Nockolds and Allen (1954). The K and Rb contents of the Hawaiian lavas have recently been determined by Lessing et al. (1963) by X-ray fluorescent spectrography, and a range of from 6 ppm for olivine basalts to approximately 120 ppm for trachytes was found. Further reference to this study will be made in the discussion of K/Rb ratios. Siedner (1965) has discussed the geochemistry of a strongly differentiated alkaline continental series of rocks from the Paresis Complex in South-West Africa, in rock types ranging from gabbros and basalts to comendites. The Rb contents of these rocks (op. cit. Table 1) are higher than the Nandewars throughout.

K/Rb ratios:

The K/Rb ratios of the Nandewar rocks can be seen in Figure 20 , where K per cent is plotted against Rb ppm, using the conventional logarithmic scales (Ahrens, 1952).

Rb^+ with an ionic radius of 1.47 Å, and K^+ with an ionic radius of 1.33 Å, show close geochemical association, since the sizes of the ions are similar and the charges are identical. The larger size of Rb^+ indicates that it should be concentrated relative to K^+ according to the Goldschmidt (1937) rules.

Taylor (1965) states that the "normal" K/Rb ratios are considered to lie in the range of 100 to 300, averaging about 230; and that any ratios outside these limits need some special explanations. This

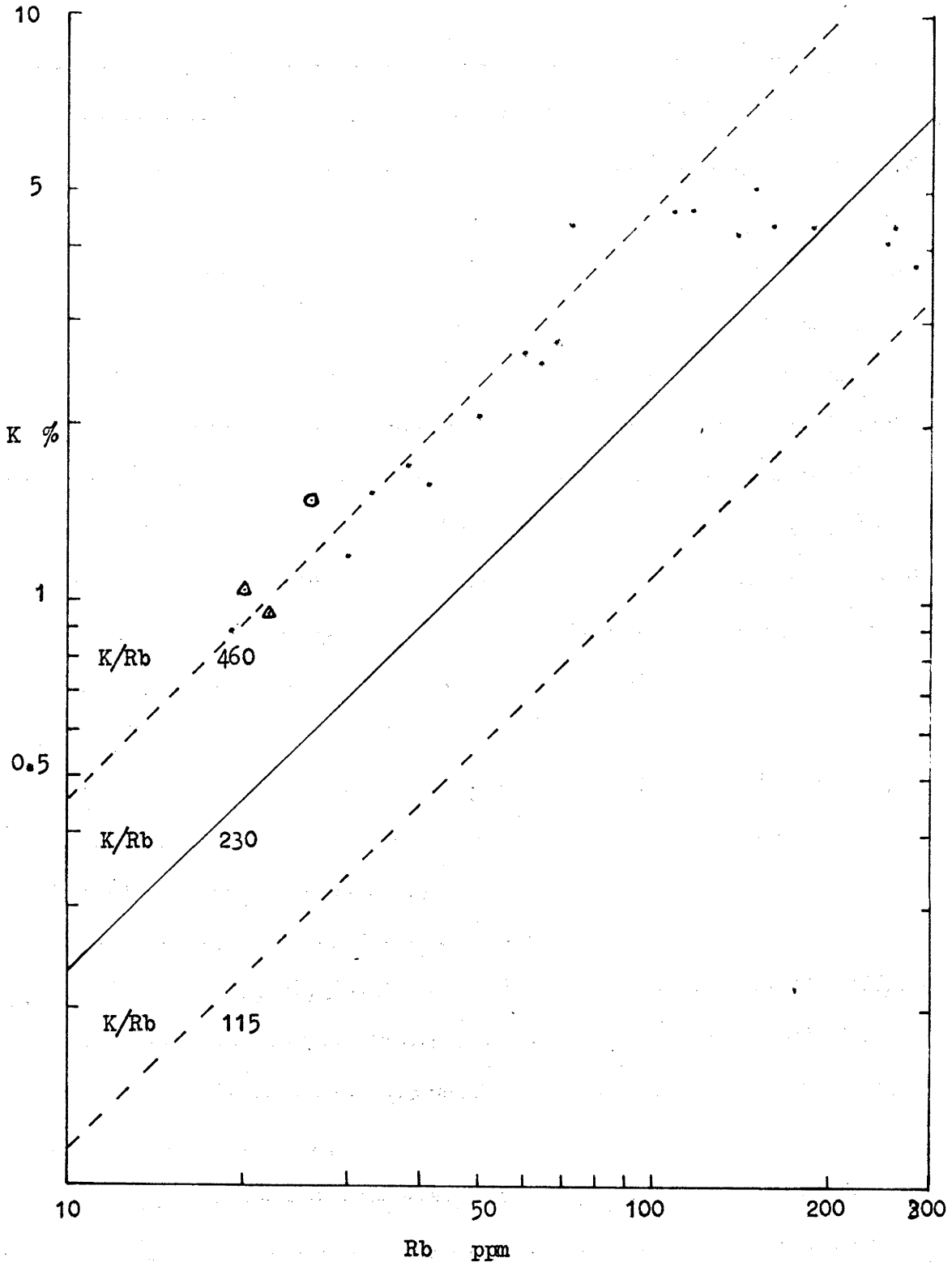

Figure 20

relation has been observed by Ahrens et al. (1952), and from the data of Nockolds and Allen (1954) and others.

In the plot of K against Rb (Figure 20) the limits for "normal" K/Rb ratios from 115 to 460 (following Ahrens et al. 1952) are plotted in dotted lines. Most of the Nandewar basic alkaline rocks have K/Rb ratios on the upper limit of the so-called "normal" ratios - i.e. 460. The K/Rb ratios observed by Lessing et al. (1963) in the low potassium lavas (K 2 per cent) from Hawaii are in the range 512 ± 11. The data of both Wager and Mitchell (1953) and Nockolds and Allen (1954) is much more variable, and the K/Rb ratios range from 120 to 1800, but an average of about 230 is indicated from Nockolds and Allen (1954). The K/Rb ratios of the basic alkaline rocks from the Paresis volcanic province (Siedner, 1965) average about 230.

As stated earlier, Taylor (1965) believes that high K/Rb ratios require some special explanation, and he states with regard to the high K/Rb ratios:

"In summary the relevant factors seem to be:

(1) The concentration of potassium is not sufficient for K-feldspar to crystallize.

(2) Barium is present in large amounts and Ba^{2+} will enter K^{+} positions preferentially.

(3) Rb^{+} is at a double disadvantage in this competition, entering only after Ba^{2+} and K^{+}.

(4) Feldspars of composition $Or_{40}Ab_{50}An_{9}Cn_{1}$ are close to the maximum of the subsolidus exsolution curve, indicating that the single feldspar phase is least stable, and cannot

tolerate much substitution of foreign ions in the lattice.

(5) If a mineral such as biotite is present, Rb will enter the large co-ordination positions, and deplete the magma".

In the basaltic Nandewar alkaline rocks with high K/Rb ratios of approximately 460, only factor (1) above could be operating, although Ba is present in moderate amounts.

The measurement of the K/Rb ratio of the Hawaiian lavas by Lessing et al. (1963), resulting in a value of 512 ± 11 indicates that, at least for the basic rocks of this province, and also possibly for the oceanic mantle, this "high" value is not abnormal.

Taubeneck (1965) suggests that the "normal" value of 240 for the K/Rb ratio (Ahrens et al. 1952; modified by Taylor et al., 1956) has little meaning, and he reaches the conclusion that mafic rocks have high K/Rb ratios and felsic rocks have low K/Rb ratios. Taubeneck further suggests that the Hawaiian basalt K/Rb ratio (512) of Lessing et al. (1963) may itself be lower than that for the oceanic mantle.

It has commonly been found that the K/Rb ratio decreases with differentiation in a magmatic sequence, due to late stage enrichment of Rb relative to K (Rb has a larger ionic radius) (Butler et al., 1962; Nockolds and Allen, 1953, 1954, 1956; Taylor et al., 1956; Taylor and Heier, 1958; Taylor, 1965). This enrichment is shown by the Nandewar alkaline series (Table 38 , Figure 20). From an initial value of approximately 460 in the basalts and trachyandesites, the K/Rb ratio decreases in the trachytes and comendites to about 160. This decrease in the K/Rb is solely due to Rb enrichment, as at this stage of

differentiation the K content is almost constant or decreasing slightly because of the increasing quartz/felspar ratio with differentiation.

Lessing et al. (1963) find that the K/Rb ratio decreases in the Hawaiian alkaline series with increasing K, from an initial value of 512 to a value of 260 in the high potassium lavas. Lessing et al. hold that this increase of K/Rb ratio is not due to magmatic differentiation, but rather is due to either a mixture of high Rb marine argillaceous material to the differentiating lava, or gaseous transfer. To support their argument these workers have presented a diagram (op. cit. Fig. 1) of K/Rb plotted against K per cent showing a constant K/Rb ratio of 512 for rocks with K up to 2 per cent. When K equals 2 per cent, a linear decrease to a K/Rb ratio of 240 (at a K value of 4 per cent occurs, due, it is postulated, to a mixture of varying proportions of material with K/Rb of 512 and 240 respectively.

Other workers on the Hawaiian lavas have not held that contamination of the differentiating lava by marine sediments has been a significant factor in the evolution of the lavas (Macdonald, 1949; Macdonald and Katsura, 1964). The data in Figure 1 of Lessing et al. (1963) could just as well be interpreted as a rather steady decrease of K/Rb during differentiation, the decrease becoming more rapid with differentiation.

The K/Rb ratios of the two Permian calc-alkaline andesites in the Nandewars are high (515 and 432). Calc-alkaline rocks are usually held to be due to the mixing of argillaceous or granitic material with basaltic magmas. Both of these contaminants are assumed to have a low K/Rb ratio. The fact that these calc-alkaline andesites can have high K/Rb ratios casts some doubt on the hypothesis of Lessing et al. (1963)

that the rocks with low K/Rb ratios in Hawaii are necessarily the result of contamination of basaltic magma.

The plot of K/Rb against K per cent (Fig. 21) for the Nandewar alkaline rocks shows that for the basic rocks (the olivine basalts, basalts, and trachyandesites) the K/Rb ratio decreases slowly as a linear function with increasing K; but as soon as the trachytic stage of differentiation is reached, the K/Rb ratio decreases sharply with no further increase in K. This indicates that the K is being held constant while the Rb is being concentrated in the late fractions.

Butler et al. (1962) point out that, as granites approach the ternary minimum in the system KAlSiO - $NaAlSiO_4$ - SiO_2, the major element composition tends towards uniformity, and only the trace element concentrations will vary. This appears to be the case in the Nandewar trachytes and comendites. From study of the felspars (Cf. section on felspars), which have approached very closely to the minimum melting composition of $Or_{35}Ab_{65}$, with very low An, further differentiation can only lead to the increase of the quartz/felspar ratio, while the felspar composition remains constant. Thus the K can only decrease slightly, but the Rb is concentrated according to the Goldschmidt rules.

The K/Rb ratios for the Nandewar alkaline series show that a high ratio, similar to the Hawaiian alkaline series, is not abnormal, and that this ratio will decrease with differentiation, this decrease becoming more rapid with late differentiates.

Using the reasoning of Taubeneck (1965), the K/Rb ratio of the upper mantle beneath the Nandewars must be at least 532, the K/Rb value for the chilled contact teschenite.

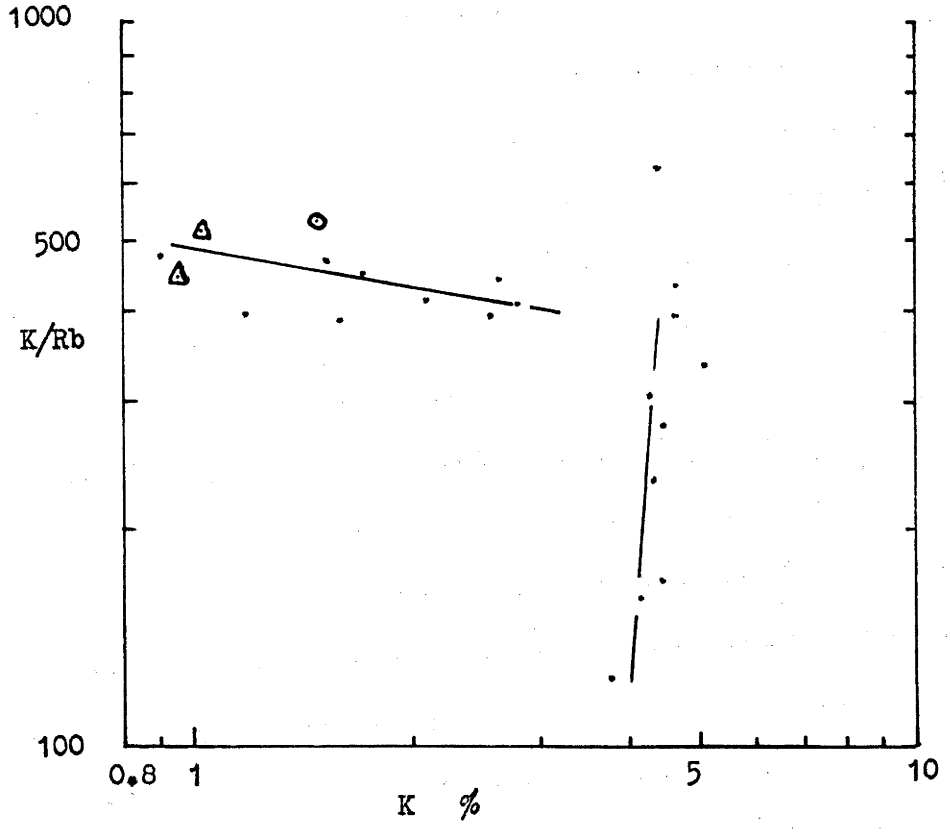

Figure 21

Doubt must be cast on the hypothesis of Ahrens et al. (1952), as pointed out by Taubeneck (1965), that the K/Rb ratio is constant for continental rocks, and that this constant is 230 (value of Taylor, 1965).

Strontium and Barium:

The Sr^{2+} content of the Nandewar olivine basalts range from 800 to 900 ppm, and the Sr falls to 600-700 ppm in the trachyandesites, to 300-500 ppm for the alkali syenite and Killarney Gap trachyte, finally being almost entirely removed in the one felspar trachytes and comendites, ranging from 1 to 15 ppm. (It has been noted in the section detailing the chemical methods that low Sr values where the Rb/Sr ratio is greater than 10/1 are subject to higher than normal error. The essential fact that the Sr values are very low, however, is still valid). This very marked depletion of Sr is quite unusual.

Nockolds and Allen (1954) record the Sr contents of several alkaline rock series, and for the Scottish Tertiary series, although the Sr is depleted in the late differentiate (5 ppm from an orthophyre), the mugearites in the middle stages of differentiation commonly have higher Sr (800-1200 ppm) than the basalts with from 300 to 500 ppm. The Hawaiian alkali basalt - trachyte series, the Polynesian alkali basalt - trachyte series, and the Polynesian alkali basalt - phonolite series also show a gradual rise of Sr with differentiation from the basaltic to the mugearitic stage followed by a fall to the trachytic stage (Nockolds and Allen, 1954). The alkaline lavas of Gough Island (Le Maitre, 1962) also duplicate this Sr trend. The Easter Island basalt - alkali rhyolite series is the only one in the literature surveyed to show the extreme type of differentiation as found in the Nandewars, and

the Sr shows a similar steady decrease from basalt to alkali rhyolite. The data for the Easter Island province is sparse, however (Nockolds and Allen, 1954, Table 15).

The strongly differentiated continental alkaline series of the Paresis Complex (Siedner, 1965) does not possess high Sr, and in these rocks the Sr decreases regularly from 350 ppm in the gabbros and basalts to 6-20 ppm in the comendites.

The Ba^{2+} of the Nandewar alkaline rocks rises from a value of about 550-850 ppm in the basalts to 1300-1500 ppm in the trachyandesites and the Killarney Gap trachyte (one basalt has 2700 ppm Ba), and is then depleted and falls from 300-450 ppm in two of the trachytes to values of from 4 to 50 ppm in the one felspar trachytes and comendites. The contact teschenite has a Ba content of 420 ppm, about half that of basalts with equivalent SiO_2 in the saturated alkaline series, Wilkinson (1959) reports even lower values for the Black Jack contact teschenites of from 275 to 325 ppm.

The late stage depletion of Ba in the Nandewar comendites is marked, but not as extreme as the Sr depletion in the same rocks.

The Scottish Tertiary alkali basalt - trachyte series, the Hawaiian alkali basalt - trachyte series, the Polynesian alkali basalt - trachyte and alkali basalt - phonolite series, as well as the Easter Island basalt - alkali rhyolite series, all show a rise of Ba in the middle to late stage of differentiation from a rather low initial value in the basalts, and a fall in the Ba in the very late stage differentiates (Nockolds and Allen, 1954).

The Nandewar alkali series does not have as low a Ba value in the basalts as other alkaline series, but because of its extreme differentiation to comendites the Nandewar late stage alkaline rocks show more extreme depletion in Ba than the examples quoted by Nockolds and Allen (1954).

The Gough Island alkaline rocks (Le Maitre, 1962) have similar Ba contents in corresponding differentiation stages to the Nandewar alkaline series. The Paresis alkaline rocks (Siedner, 1965) show an overall decrease of Ba with differentiation, but this tend is irregular.

The extreme depletion of both Sr and Ba in the late differentiates of the Nandewar alkaline rocks is not seen in any of the quoted examples of geochemically studied alkaline series, mainly because these series lack the extreme differentiates seen in the Nandewars.

Calcium - strontium relations:

Heier and Taylor (1959) state that Sr^{2+} (radius 1.18 Å) is often regarded as a close associate of Ca^{2+} (radius 1.02 Å), but it can show a close association with Ba^{2+} (radius 1.34 Å) particularly in potash felspars. Since the Sr can substitute for two elements, Heier and Taylor (op. cit.) do not expect a simple relationship to exist. If Sr^{2+} is camouflaged by Ca^{2+}, it should be concentrated relative to the Ca because of the larger size of the Sr^{2+} ion. The Sr has been found to enter the plagioclase (Wager and Mitchell, 1951) and does not enter pyroxene to any extent, although Wilkinson (1959) reports 150 to 175 ppm in clinopyroxenes from the Black Jack teschenites. Wilkinson further finds up to 4000 ppm Sr in apatites, and it appears that this mineral is favourable for the acceptance of Sr.

From the basalts and trachyandesites in the Nandewar alkaline province, the Sr/Ca ratio remains constant or even rises slightly with differentiation. The absolute amount of Sr falls, because some is being removed in the potash felspar component of the ternary felspars, and also in the apatite, which is a common constituent of the trachyandesites. Because Ca is being removed from the magma by plagioclase and clinopyroxene, the Sr/Ca ratio remains reasonably constant. As soon as potash felspar becomes a significant component of the felspars, in the calcic anorthoclases, and later in the sanidine-anoorthoclase cryptoperthites, the Sr is captured by the potash felspar component, and is almost completely removed from the magma. The Ca is not depleted at the same rate, and the Sr/Ca ratio falls rapidly in the trachytes and comendites. Heier and Taylor (1959) find that the Sr/Ca ratio is ten times as great in K felspar than in plagioclase, indicating that Sr enters K felspar more readily than plagioclase.

In the alkaline suites studied by Nockolds and Allen (1954), the Sr/Ca ratios rise in the early to middle stages of differentiation, then fall at the trachytic stage of fractionation. None of the suites studied has as great a fall in the Sr/Ca ratio as in the Nandewar alkaline rocks, because none of them are so depleted in Sr. The Gough Island alkaline series (Le Maitre, 1962) shows similar behaviour in Sr/Ca ratios.

Barium - potassium relations:

Taylor (1965) states that Ba^{2+} (radius 1.34 Å) substitutes only for K^{+} (radius 1.33 Å) among common cations. The Ba, because of its similar size, but higher charge, should be captured by early forming K minerals.

In the Nandewar alkaline rocks, the Ba content rises with differentiation from basalts to trachyandesites from an average value of 750 ppm to about 1400 ppm. Since there are no significant amounts of potash-bearing phases in the basalts, the Ba will be concentrated in the trachyandesites where significant amounts of K felspar occur in the ternary felspars in the potash oligoclases and calcic anorthoclases. Here the Ba is rapidly captured by the K felspar, and is effectively removed from the magma. The Ba content of the trachytes and comendites is low, and except for one rock (73-5) does not rise above 50 ppm.

The Ba/K ratio rises in the early to middle stages of differentiation, although this rise is small. Once K felspar becomes a significant component of the ternary felspars, the Ba is removed, and the Ba/K ratio falls rapidly, becoming quite low in the trachytes and comendites.

This behaviour is duplicated by the alkaline series studied by Nockolds and Allen (1954), the Gough Island alkaline rocks (Le Maitre, 1962), and by the Paresis Complex alkaline rocks (Siedner, 1965).

Ba/Sr ratios:

Siedner (1965) has suggested that a closer association should be expected between Sr and Ba than between Sr and K, on the basis of similar charge and ionization potentials. He considers (op. cit., p. 125) that if the Ba content is high, it tends to behave as a major element towards Sr, and exerts a significant control over its distribution.

The smaller size of the Sr^{2+} ion (radius 1.18 Å) relative to the Ba^{2+} ion (radius 1.34 Å) indicates that, according to the Goldschmidt rules, the Sr should be removed before Ba, and that the Ba/Sr ratio

should rise with differentiation.

The Ba/Sr ratios of the Nandewar alkaline rocks do rise during differentiation, and Ba and Sr show a very marked co-variance. This feature has also been noted in the Paresis Complex alkaline rocks (Siedner, 1965). Heier and Taylor (1959) find marked co-variance of Ba and Sr in alkali felspars from Norwegian Precambrian gneisses, granites, and pegmatites, but they state (op. cit., p. 299) "... it can be seen that the Ba/Sr ratios are not constant and that the ratio decreases as the absolute concentration of the two elements falls."

The Ba/Sr ratios of the Scottish Tertiary alkali basalt - trachyte series, the Hawaiian basalt - trachyte series, and the Polynesian basalt - trachyte series increase with differentiation (Nockolds and Allen, 1954), as do the Ba/Sr ratios for the Gough Island series (Le Maitre, 1962).

Heier and Taylor (1959) conclude, for the alkali felspars from Precambrian gneisses, granites and pegmatites, that the relative decrease of Ca, Sr, and Ba is in the order Ca < Sr < Ba. For the Nandewar alkaline series, the relation is Ca < Ba < Sr, and the Sr/Ca ratios decrease and the Ba/Sr ratios increase, respectively, with differentiation.

The discrepancy between these results appears to be due to the variable behaviour of Sr^{2+}, which can substitute for either Ca, K, or Ba.

Zirconium:

Taylor (1965) states that no common cation (except Fe^{2+}) is close

in size to Zr^{4+} (radius 0.79 Å) and that it tends to form a separate mineral phase, zircon (Zr_2SiO_4).

The Zr of the Nandewar alkaline rocks rises steadily from values 120 to 200 ppm in the basalts to a maximum of from 700 to 1400 ppm in the trachytes.

High Zr concentrations are typical of alkaline series, and in all the alkaline series of rocks studied by Nockolds and Allen (1954), the Zr rises steadily with differentiation, a feature also recorded in the Gough Island alkaline rocks (Le Maitre, 1962).

Wager and Mitchell (1951) have stated that zirconium is very soluble in alkali rich magmas, and they estimate that zircon is precipated when the amount of Zr rises to 300 or 400 ppm. Wager and Mitchell further state that Zr replaces Ca in pyroxenes, while Degenhardt (1957) believes that Zr replaces $NaFe^{3+}$, the Zr being captured by the Fe^{3+}. Taylor (1965) believes that the Zr can substitute to some extent for Ti^{4+}, and hence can accompany that element in substituting for Fe^{3+}.

Wilkinson (1959) records 200 to 225 ppm Zr in clinopyroxenes from the Black Jack clinopyroxenes. No zircon crystals can be observed in the olivine basalts from the Nandewars, and it is suggested that up to about 250 ppm the Zr enters the clinopyroxene, but above that amount zircon will form as a discrete phase. When the clinopyroxene decreases in amount in the trachytes and comendites, all the Zr will enter the zircons.

A plot of Zr against $\frac{Na + K}{Na + K + Ca} \times 100$ (Figure 22) reveals a

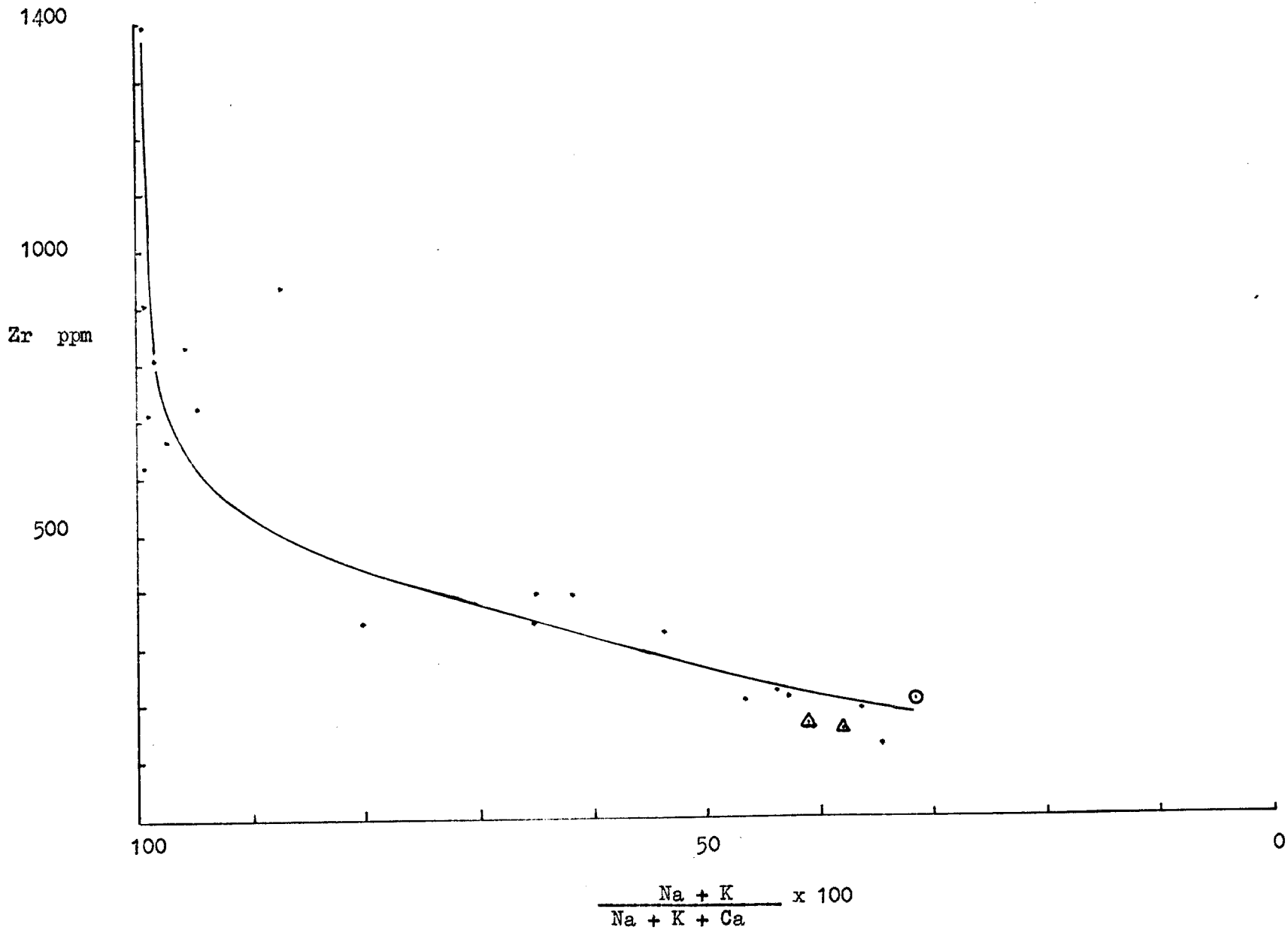

Figure 22

steady enrichment in Zr up to a $\frac{Na + K}{Na + K + Ca} \times 100$ ratio of 95, and then a very rapid increase of Zr occurs for a small increase in the $\frac{Na + K}{Na + K + Ca} \times 100$ ratio. This trend is the same type as that in the alkaline rocks of the Paresis Complex (Siedner, 1965).

The Th/Zr x 10^2 ratio has been calculated for the Nandewar alkaline series, and this ratio is remarkably constant, rising slightly with differentiation, and Th and Zr show marked co-variance.

Adams et al. (1959, p. 310) state "The ionic radii, high valencies and electronegativities of thorium, uranium, cerium, zirconium, and hafnium make them a unique and cohesive group that, by virtue of these properties, cannot form significant isomorphic series involving major rock-forming minerals. Instead these five elements tend to be segregated into very minor accessory phases that are dominated by the more abundant zirconium and cerium." They further state that zircon can contain a few percent of U and Th which is present either as simple ionic substitution as tetravalent ions, or as optically continuous thorite, $ThSiO_4$.

Since zirconium (0.79 Å) and hafnium (0.78 Å) have ionic radii about 15 per cent less than Th (1.02 Å) and U (0.97 Å), it would be expected that the Th and U would be concentrated relative to Zr in late fractions. This is the observed relation between Th and Zr in the Nandewar alkaline rocks. Since the ionic radius of U is closer to Zr than Th, U is not concentrated as much relative to Zr as Th.

<u>Potassium, Thorium and Uranium:</u>

As stated earlier, gamma ray spectrometric analyses have been

carried out for K. U, and Th on selected alkaline rocks from the Nandewar province. These analyses were carried out by Dr. K.S. Heier. Only brief comment on the analyses will be made here.

The U, Th, and K values, with the Th/U, Th/K x 10^4 and U/K x 10^4 ratios are set out in Table 39 , and the graphs of U ppm against K per cent, Th ppm against K per cent, and Th ppm against U ppm are plotted in Figures 23 , 24 , and 25 respectively.

Heier et al. (1964) have studied the Th, U, and K in Hawaiian lavas and reach the following conclusions (p. 258):

"(1) A strong coherence between thorium, uranium and potassium exists in most rock types.

(2) The concentrations of thorium, uranium and potassium increase with petrogenic evolution, and the relative enrichment is thorium > uranium > potassium, resulting in an increase in the thorium/potassium, uranium/potassium and thorium/uranium ratios.

(3) During normal magmatic fractionation the variation in the ratios of these elements do not exceed one order of magnitude."

The conclusions of Heier et al. (1964) are valid also for the alkaline rocks studied in the Nandewars, although differences in detail are due to the extreme fractionation present in the Nandewar trachytes and comendites.

The U varies from 0.7 ppm in an olivine basalt to from 5.2 ppm to 6.2 ppm in the trachytes; the Th varies from 2.2 ppm in the olivine basalts to from 20 ppm to 40 ppm in the trachytes and comendites,

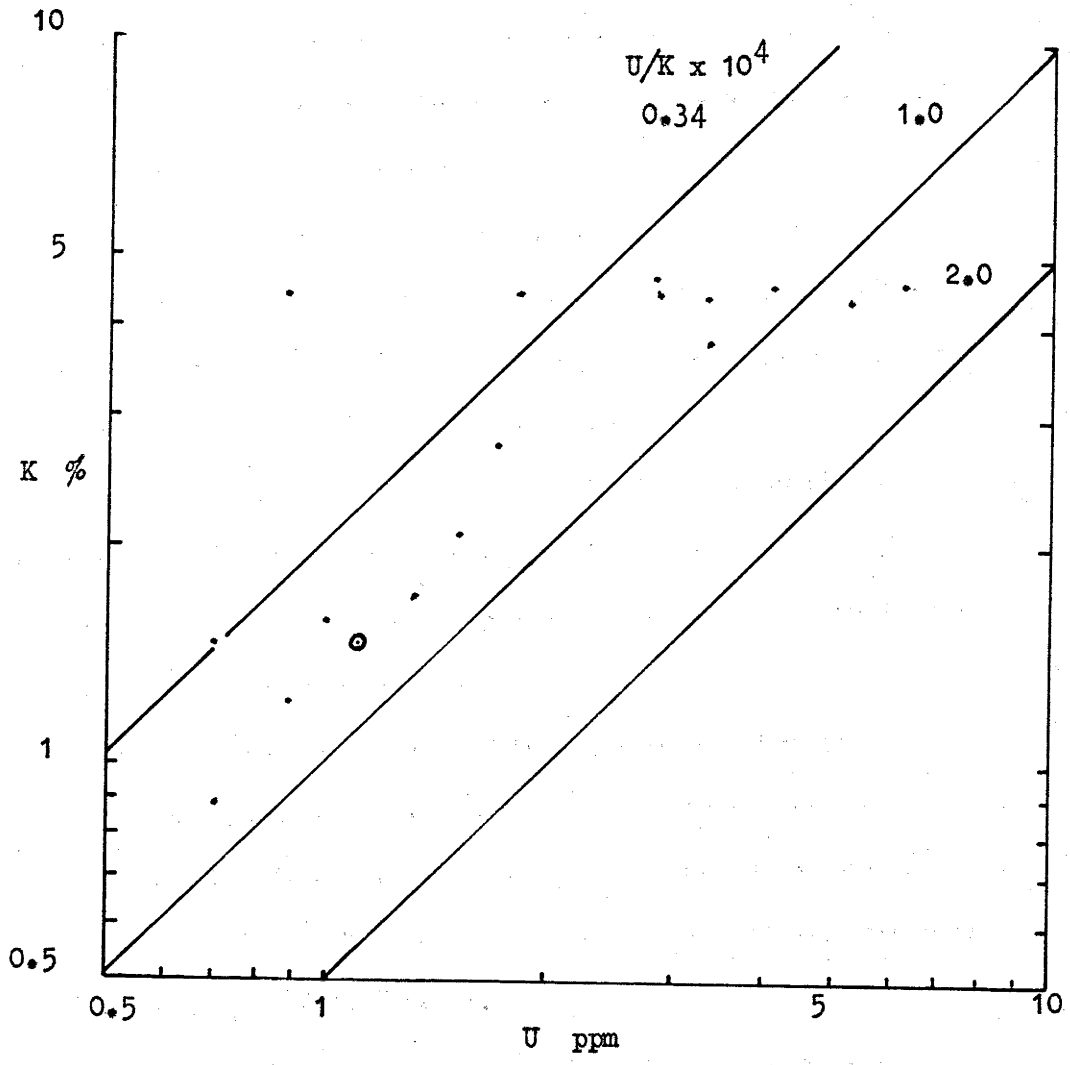

Figure 23

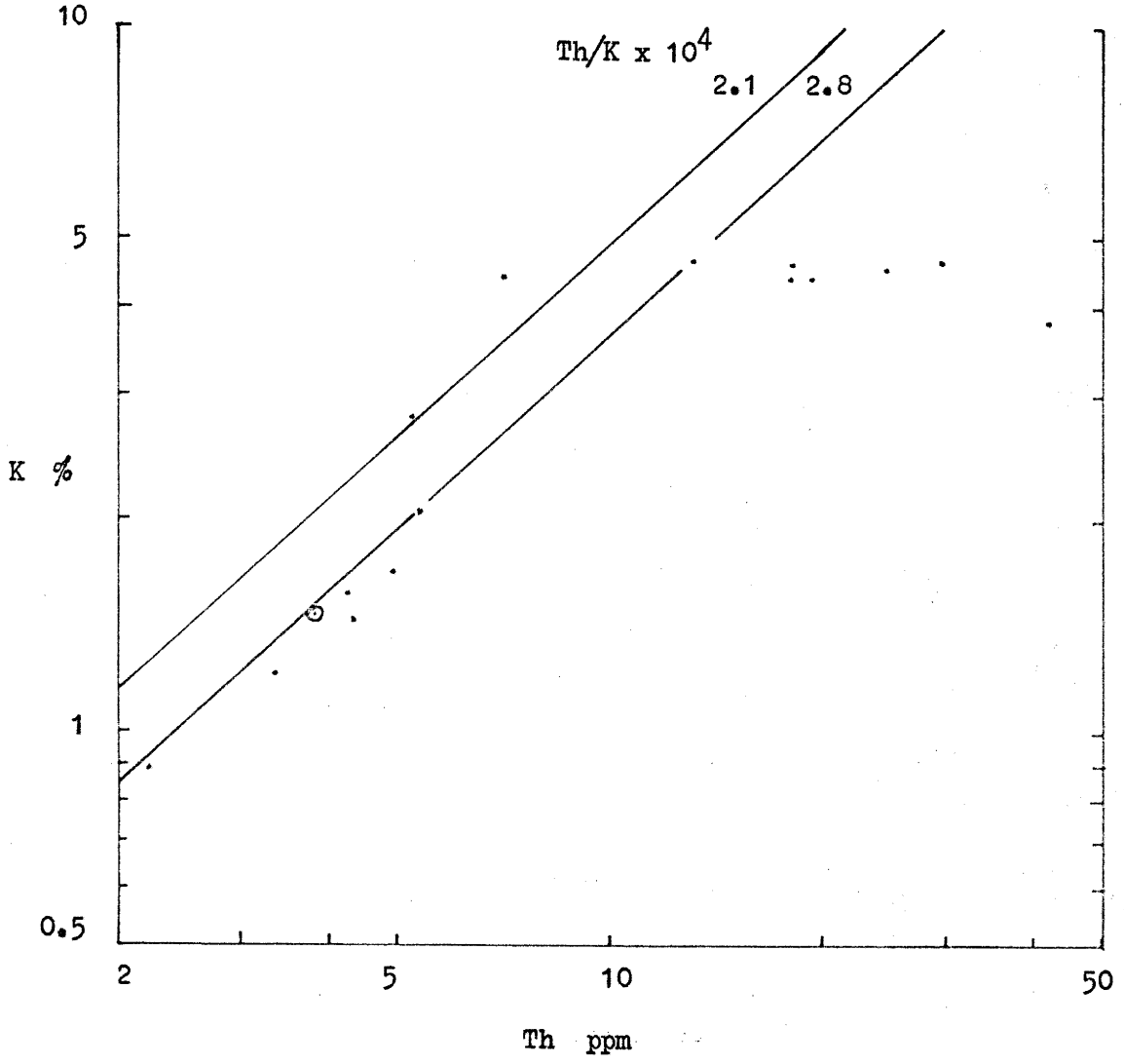

Figure 24

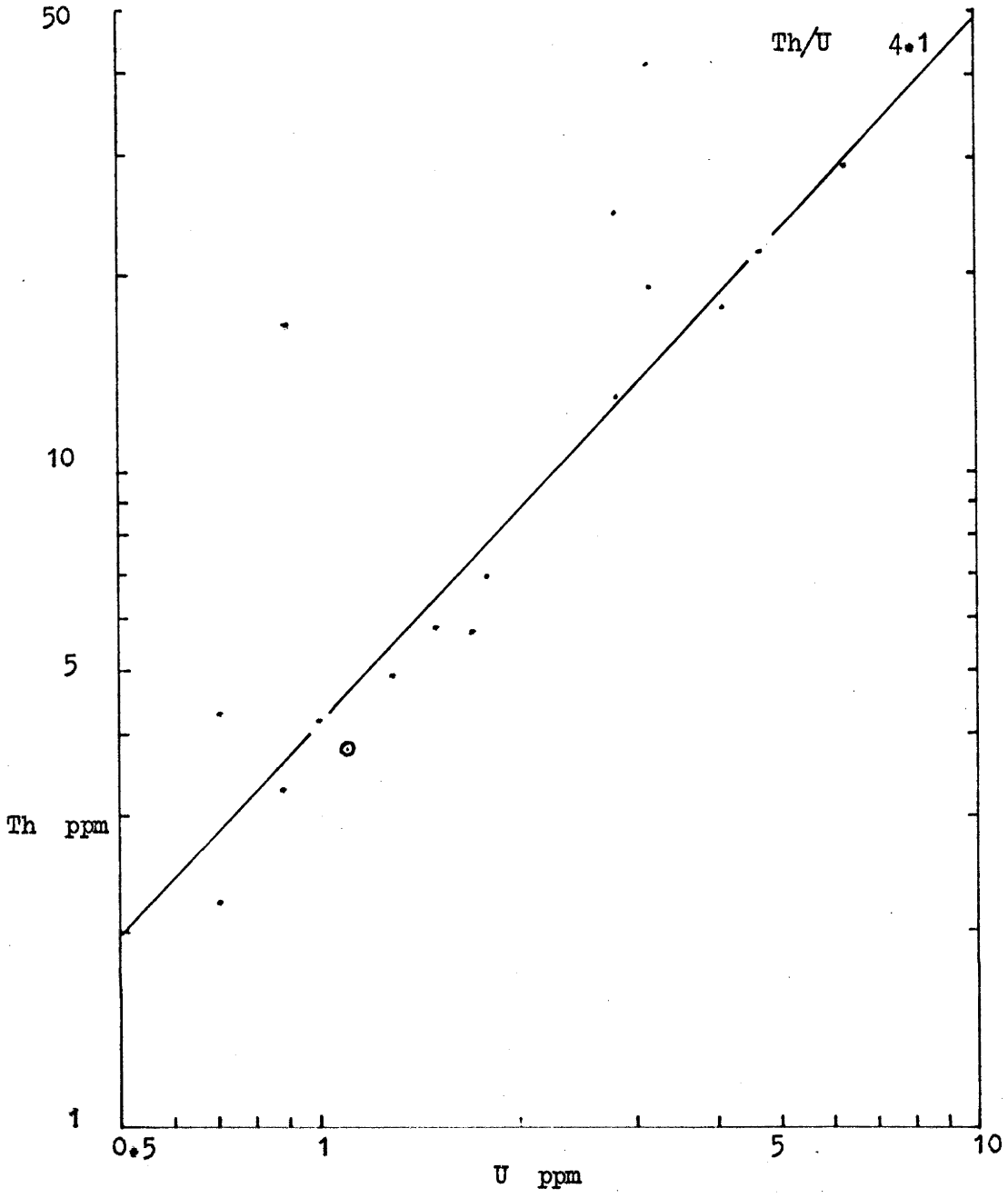

Figure 25

and the K increases from 0.9 per cent to a maximum of 4.7 per cent in the trachytes.

The U/K x 10^4 ratios are reasonably constant for the olivine basalts, basalts and trachyandesites (0.61 - 0.79) but increase in the trachytes and comendites, ranging up to 1.7 (cf. Fig. 23). This increase in the U/K ratio occurs because the K is nearly constant in the trachytes and comendites, but the U increases steadily.

The Th/K x 10^4 ratios are steady at about 2.8 in the olivine basalts, basalts, and trachyandesites, but rise in the trachytes, ranging up to 11 (cf. Fig. 24), this rise also being due to steady K values with rising Th.

This rise in both the U/K and Th/K ratios occurs at the same point at which the K/Rb ratios begin to decrease sharply, and the same explanation is offered: at the trachytic and comenditic stage of fractionation the K content is held constant because the alkali felspar has reached the minimum melting composition, and this remains constant with further fractionation.

The Th/U ratio increases steadily with differentiation (cf. Fig. 25); although there are some anomalously high Th/U ratios among the trachytes. This rise in Th/U ratios is due to the concentration of Th relative to U, a result of the larger size of Th^{4+} (radius 1.02 Å) than U^{4+} (radius 0.97 Å), and occurs according to the Goldschmidt rules. The strong association and co-variance of Zr and Th, and also Zr and U, indicates that the U and Th substitute as tetravalent ions in the zircons, and U will be accepted into this mineral before Th.

PETROGENESIS

PETROGENESIS

Introduction

In this Section, various petrogenetic aspects of the alkaline volcanics are discussed. The relative stability of the ferromagnesian minerals in the peralkaline trachytes, in particular the cossyrite, has been related to the synthetic stability data now available (Ernst, 1962). The reasons for the development of peralkalinity in the trachytes is also discussed, and finally the relation between the teschenites and the saturated alkaline series and their respective differentation trends, are compared and contrasted. Some conclusions as to the age of the Nandewar volcano have been drawn.

Stability of the ferromagnesian phases in the peralkaline trachytes:

The relative stability of the ferromagnesian minerals in the cossyrite trachytes, and the oxidation conditions under which they have crystallised can be considered in relation to experimental data (Ernst, 1962). In Ernst's study, the stability of riebeckite - arfvedsonite solid solutions crystallised from the bulk composition $Na_2O.5FeO_x.8SiO_2$ + excess H_2O (where x varies from 1.1 to 1.2) under various conditions of oxygen partial pressures and various fluid (H_2O) pressures were determined. Synthetic Ti-free aenigmatite was found in runs with P_{H_2O} less than 1,000 bars and partial pressures of oxygen defined by the magnetite - wüstite and wüstite - iron buffers. The field stability of aenigmatite is defined on the low temperature side by the reaction of fayalite + acmite to aenigmatite + quartz + O_2, and on the high temperature side by the incongruent melting of aenigmatite (+ quartz + fluid) to fayalite + melt + oxygen. As Kelsey and McKie (1964) note, the stability field of natural Ti-bearing cossyrite

will be larger than that of the synthetic Ti-free aenigmatite. Furthermore, the addition of CaO, which can enter the ferromagnesian phases hedenbergite, arfvedsonite and katophorite would also alter stability relations. It would be expected that with the addition of CaO to the synthetic system investigated by Ernst (op. cit.), hedenbergite would form in roughly the same field as fayalite. The bulk composition used by Ernst is also Al free. From an inspection of the stability diagrams of Ernst (1962, Fig. 6 - 12C) the following relations with falling temperature (assuming a constant or falling partial pressure with falling temperature) are assumed to exist:

For bulk compositions with relatively high CaO:

1. At high partial pressures of oxygen (in the region defined by the magnetite - hematite buffer):

Magnetite with ilmenite (either in solid solution or as a discrete phase), hematite or maghematite (Buddington and Lindsley, 1964) followed by aegerine, and finally riebeckite.

2. At low partial pressures of oxygen (in the region defined by the magnetite - wüstite and wüstite - iron buffers):

Ulvöspinel-rich magnetite, followed by hedenbergite, cossyrite, and finally katophoritic amphibole.

For bulk compositions with relatively low CaO:

1. At high partial pressures of oxygen (defined by the magnetite - hematite buffer):

Magnetite, with ilmenite, hematite or maghematite, followed by acmite and finally riebeckite.

2. At low partial pressures of oxygen (defined by the magnetite - wüstite and wüstite - iron buffers):

Ulvöspinel-rich magnetite, followed by fayalite, cossyrite, and finally arfvedsonite.

If equilibrium conditions of crystallisation were realised, reaction of each of the phases would occur, and only the lowest temperature members would remain (the alkali amphiboles). If non-equilibrium conditions prevailed (the common condition in volcanic rocks) a reaction series as proposed by Upton (1964) would exist.

The ferromagnesian assemblages encountered in the Nandewar alkaline trachytes are:

1. Magnetite - hedenbergite - cossyrite - riebeckite - arfvedsonite solid solution.
2. Magnetite - hedenbergite - acmite solid solution - cossyrite - riebeckite - arfvedsonite solid solution.
3. Titanomagnetite - hedenbergite - acmite solid solution.
4. Magnetite - hedenbergite - acmite solid solution - cossyrite - katophoritic amphibole.
5. Riebeckite - arfvedsonite solid solution alone.

The occurrence of hedenbergite places assemblage 1 in the high calcium - low partial pressure of oxygen class outlined above; assemblage 2 is intermediate between the low and high CaO classes, still with low P_{O_2}, but higher than assemblage 1; assemblage 3 is in the high CaO class, with P_{O_2} between the high and low values (the hedenbergite-acmite composition is assumed to be rather similar to the analysed hedenbergite from trachyte GOV4, as this assemblage occurs in a rock of the same assumed

bulk composition as GOV4, and is in the same flow); assemblage 4 has formed under similar conditions to assemblage 2, except that the P_{O_2} prevailing when the katophorite crystallised was lower and the temperature was higher (Miyashiro, 1957) than that of the equivalent stage of assemblage 2; and assemblage 5 has formed by slower cooling at low partial pressures of oxygen with rather low content of CaO (it is significant that the rock containing this assemblage 100-6 forms a large body, and has coarser microsyenitic patches, indicating slow cooling).

Carmichael (1962) believes that the assemblage fayalite + ilmenite is antipathetic to the existance of cossyrite, and suggests that a reaction relationship may exist, and that with increasing partial pressures of oxygen the amount of pyroxene precipitating, and its soda content, should increase, as well as increasing the amount of magnetite and possibly ilmenite at the expense of fayalite and cossyrite (op. cit., p. 108).

The assumed stability relations for both relatively high - CaO compositions (Fig. 26) and relatively low Ca composition (Fig. 27) for the Ti bearing ferromagnesian phases have been drawn, being based on the stability of synthetic Ti and Ca-free phases crystallised from the bulk composition $Na_2O.5FeO_{1.1-1.2}.8SiO_2$ + excess H_2O, as deduced by Ernst (1962).

The field of stability of the amphiboles shown in the diagram of Ernst (op. cit., Fig. 11B) does not consist of one constant amphibole composition, but consists of compositions varying in a regular manner with temperature and partial pressure of oxygen, and Ernst indicates that in the lower P_{O_2} higher temperature portion of the amphibole field, the composition approaches arfvedsonite, and as the P_{O_2} rises and temperature

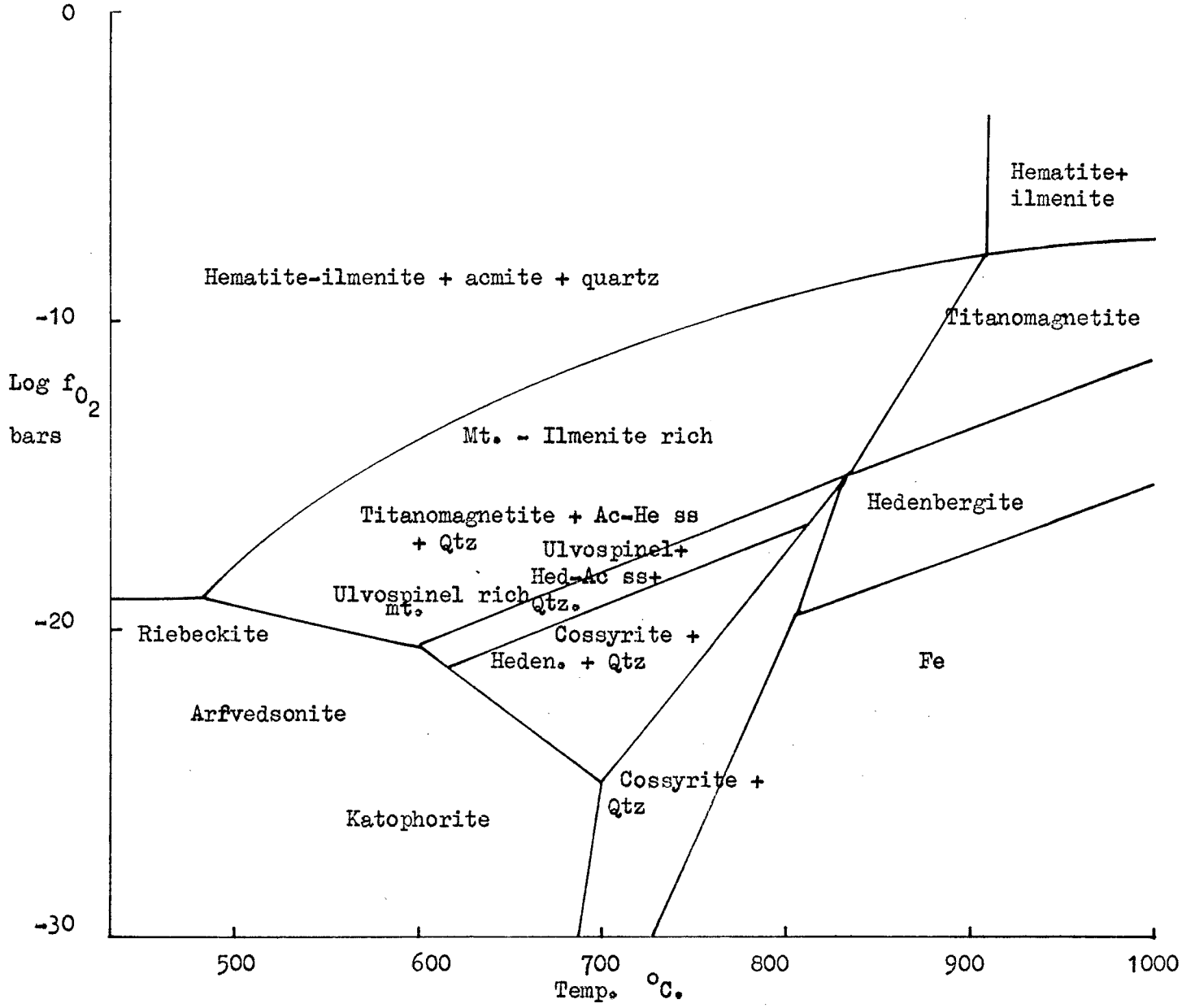

Figure 26

Suggested stability relations for relatively high Ca, Ti bearing compositions in the system $Na_2O.\ 5FeO_x + 8SiO_2 + xs\ H_2O$. Modified and simplified after Ernst (1962).

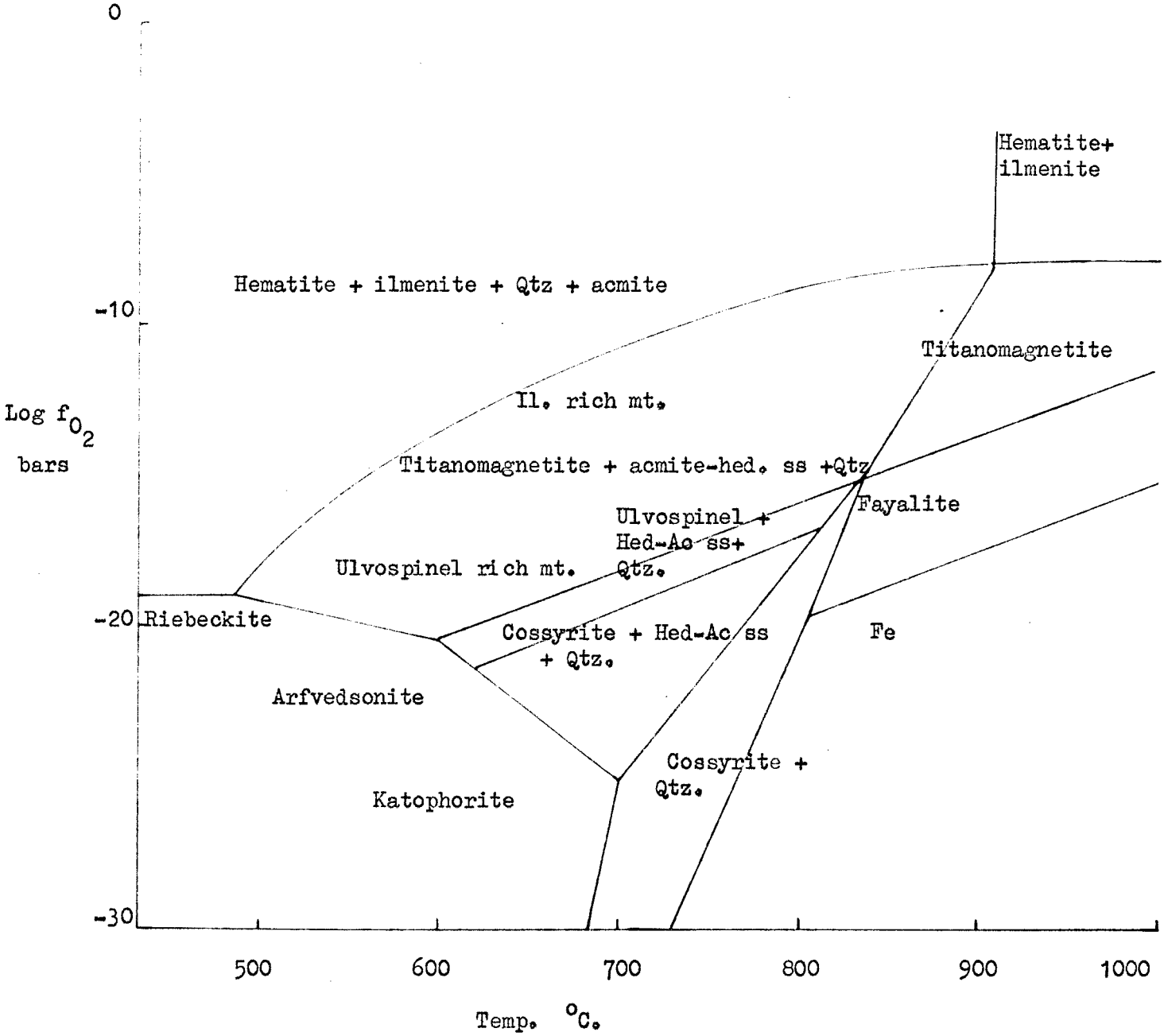

Figure 27

Relatively low Ca, Ti bearing compositions in the system $Na_2O.5FeO_x8SiO_2$ + xs H_2O, and the suggested stability relations. Modified and simplified after Ernst (1962).

falls, the amphiboles become richer in riebeckite. With the addition of CaO to the system, a katophoritic amphibole ($Na_2CaFe_4^{2+}Fe^{3+}Si_7Al\ O_{22}(OH)_2$; Deer, Howie and Zussman, 1963, vol 2) can form. Miyashiro (1957) indicates that katophorite forms at a higher temperature than arfvedsonite, and the lower content of Fe^{3+} in katophorite, compared to arfvedsonite, indicates a lower P_{O_2} for katophorite formation than for arfvedsonite. Thus katophorite would form at the high temperature, low P_{O_2} end of the amphibole stability field (Ernst, 1962, Fig. 12), and the postulated relations are shown in Figs. 26 and 27 in this thesis.

For the high CaO stability diagram (Fig. 26), the field of hedenbergite is shown as separate from that of acmite, but there would be a continuous gradation in composition between the two pyroxenes. With falling temperature and rising P_{O_2} the pyroxene would be enriched in acmite. There is extensive, if not complete, solid solution between hedenbergite and acmite (Yagi, 1962; and from the recorded occurrence of homogeneous clinopyroxene of the approximate composition $Ac_{50}He_{50}$ in this study).

Bailey (1963) states that acmite may possibly break down with falling temperature to give a stable amphibole field, a relation indicated by the work of Ernst (1962), where, with falling P_{O_2} and temperature the amphibole stability field is reached from a field of acmite stability.

Peralkalinity in the trachytes:

The development of peralkalinity in alkaline series is a problem which has engaged the attention of many petrologists. Carmichael and MacKenzie (1963) have stated the problem: the strongly peralkaline pantellerites have developed by differentiation from peraluminous trachytes in Pantelleria.

Bowen (1945) has noted that in the system albite - nepheline - wollastonite pure albite fails to crystallise in liquids containing a lime-bearing component, and plagioclase forms rather than albite, and this phenomenon has been termed the "plagioclase effect". This "plagioclase effect" will apply in any synthetic system containing an albite component and a Ca-bearing component, the CaO will be preferentially taken up by plagioclase, and the resulting liquids will trend towards undersaturation of Al_2O_3 with respect to alkalies (peralkalinity). Carmichael and MacKenzie (1963) have shown the theoretical consequences of the "plagioclase effect" for liquids of trachytic composition in the Di-An-Ab system. The liquids, which lie on the Ab-Di join at the 95 per cent Ab - 5 per cent Di pseudo-eutectic point, will leave this binary join and become enriched in sodium silicate because of the failure of pure albite to crystallise. Bailey and Schairer (1964) are of the opinion that the "plagioclase effect" only operates if there is a molecular excess of Na + K + Ca over Al, that is, if there is no normative corundum in the rock.

Carmichael (1964) has found a natural example of this "plagioclase effect" from a kenyte, where an initial liquid with 5.8 per cent normative An has precipitated abundant, relatively An-rich felspar, of composition $Or_{17}Ab_{63}An_{20}$, leaving a residual liquid which is peralkaline, having 4.2 per cent normative acmite. This rock is strongly undersaturated, but the "plagioclase effect" should also act in oversaturated systems.

In the Nandewar oversaturated alkaline rocks, it has been observed that the analysed felspar phenocrysts have more An than the bulk normative felspar compositions. The relevant data is set out below:

Rock No.	24	GOV4	KG
Bulk rock peralkalinity ratio	1.07	1.14	0.80
Bulk norm. felspar			
or	38.0	41.6	42.0
ab	62.0	58.4	55.6
an	0.0	0.0	2.4
Analysed felspars			
or	40.3	39.5	42.2
ab	58.9	59.9	54.3
an	0.8	0.6	3.5
or	37.4	39.9	40.0
ab	61.4	59.1	55.9
an	1.2	1.0	4.1
or			33.9
ab			58.2
an			7.9

The bulk rock compositions of trachytes 24 and GOV4 are peralkaline. A similar situation exists in these trachytes as Carmichael (1964) had described for the undersaturated kenyte, although the felspars are less enriched in An. The Ca going into the felspars is withdrawn from the normative ferromagnesian minerals (the pyroxenes) which become enriched in alkalies, and the modal minerals such as alkali pyroxenes, alkali amphiboles and cossyrites crystallise.

The data for the peraluminous trachyte KG is also tabulated. Here the felspars are also richer in An than the normative felspar component of the rock (although this normative An is low because of the formation of

normative calcite, as explained before, the modal carbonate is most likely sideritic), but this has not produced peralkalinity in the rock. The continuance of this "plagioclase effect" results in peralkaline cossyrite trachytes such as 24 and GOV4.

Carmichael and MacKenzie propose that the "plagioclase effect" no longer operates once the liquids become peralkaline, and any calcium remaining in the liquid is incorporated in clinopyroxenes. Bailey and Schairer (1964), however, believe that the "plagioclase effect" does not cease to be viable when alkali excess is achieved. The formation of the anorthite molecule will be severely inhibited in a peralkaline liquid, but not stopped.

The comendites in the Nandewars are either just peraluminous or just peralkaline - theoretically the peralkalinity ratio should be no greater than 1, since the rocks merely consist of alkali felspar and quartz. It would appear that the "plagioclase effect" ceases when the Ca content of the magma is very low, as in these comendites. The reason why peralkaline liquids should develop (giving cossyrite trachytes), and then with further differentiation liquids which are not peralkaline at all (giving the comendites) is not clear.

The withdrawal of large amounts of plagioclase in the 'big felspar' basalts in the early stages of differentiation undoubtedly removes large amounts of Al_2O_3 from the magma, and should enhance the ultimate development of peralkalinity, or at least initiate this trend. Bailey and Schairer (1964) envisage a similar situation existing for alumina saturation and undersaturation as that which exists for silica saturation and undersaturation - a slight excess of alumina over Na + K + Ca will be accentuated

with differentiation, and similarly a deficiency of alumina will also be accentuated with fractionation. In the latter case, an excess of alkalies alone over alumina should develop because of the "plagioclase effect".

The two alkaline rock types and their differentiation:

The scarcity of olivine basalts, and their differentiated nature, is quite unusual, and is not found in many of the volcanic alkaline provinces on which work has been published.

The chilled contact teschenite is strongly undersaturated and quite basic. Differentiation of similar teschenites leads to strongly undersaturated derivatives, analcite syenites (Wilkinson, 1958), the felsic normative components of which plot in the undersaturated low temperature trough of the SiO_2-$NaAlSiO_4$-$KAlSiO_4$ system (Bowen, 1937b), petrogeny's "residua system", falling on the $NaAlSiO_4$-$KAlSiO_4$ side of the $NaAlSi_3O_8$-$KAlSi_3O_8$ join. The analcitite shows some of the features of this differentiated composition. Furthermore, the occurrence of nepheline in the norm of the teschenite places the composition on the silica-poor side of the critical plane of silica undersaturation of Yoder and Tilley (1962, Fig. 1) in the Di-Qz-Fo-Ne tetrahedron. Yoder and Tilley (op. cit.) state that a nepheline normative rock could by oxidation pass into hypersthene and quartz normative types. It is true that the oxidation ratio of the olivine basalt Gr 1 from the saturated (hy normative) alkaline series ($Fe_2O_3/Fe_2O_3 + FeO = 37.5$) is higher than that for the contact teschenite CTS (23.3). However, the CaO and MgO is higher in the teschenite than in the olivine basalt, and pyroxene and olivine would have to be removed from the teschenite magma to give a basalt of the composition of Gr 1, but as noted before, removal of these phases leads to an undersaturated alkaline residuum. The trace element

data (in particular the Ba) casts doubt on the derivation of the saturated olivine basalts from a magma of teschenite composition. It is therefore concluded that the teschenite and analcitite have been derived from a different magma than that which is the parent of the saturated alkaline series. The teschenite has been intruded at an earlier stage than the extrusion of the saturated alkaline volcanic rocks (in some cases the teschenite sills have been intruded by trachyte dykes). The statement of Wilshire and Binns (1961, p. 186) that the analcitite sill with ultrabasic xenoliths is one of the feeders to the alkaline lavas and plugs of the Nandewar Mountains is regarded as incorrect.

This does not rule out the possibility that the teschenites and analcitites on the one hand, and the saturated alkaline series on the other, could have been derived from a common parent material at depth in the mantle. Yoder and Tilley (1962) and Kushiro and Kuno (1963) have both outlined processes by which a single parent basic material, either eclogitic or peridottitic, could give both saturated (tholeiitic and saturated alkaline basalts) and undersaturated (nepheline normative basalts) derivatives. No process occurring at the surface or in the upper crust seems capable of accounting for the differences between the two types, or the transition between them.

Macdonald (1949) has proposed that the olivine and clinopyroxene rich rocks in Hawaii have formed by the gravitative settling of olivine and clinopyroxene in the magma chamber, the subsequent tapping of this layer resulting in eruption of oceanites and ankaramites. The scarcity of olivine basalts in the Nandewar province suggests that a layered magma chamber existed, and that only the uppermost levels have been tapped. The occurrence of phenocrysts in the olivine basalts and 'big felspar' basalts indicates

that there was a period of intratelluric crystallisation. The long period of tectonic stability in the crust in the region of the Nandewar Mountains would have enhanced settling of phenocrysts in a subjacent magma chamber. The eruption of the 'big felspar' basalts with abundant phenocrysts of plagioclase suggests the existence of a region in the magma chamber enriched in plagioclase. Macdonald (1949) notes that removal of olivine in excess of stoichiometric proportions could yield quartz normative derivatives.

After the eruption of the basalts and trachyandesites which formed the shield volcano, there was a long period of erosion to form the erosion caldera. Both Edwards (1935, 1938a) and Macdonald (1949) propose that small satellitic, cupola like chambers developed in Victoria and Hawaii, respectively in which further differentiation was greatly enhanced. Increasing pressure of volatiles in these chambers would eventually force intrusion into overlying structural weaknesses. Edwards (1938a) further postulates that anorthoclase phenocrysts will rise to the top of these chambers, and will appear in the trachytic rocks subsequently extruded and intruded into higher levels of country rock. The appearance of anorthoclase phenocrysts in some of the trachytes of the Nandewars with features suggesting intratelluric crystallisation and disequilibrium with the magma in which they were enclosed, supports this view.

The restriction of the extremely differentiated comendites in the Nandewards to the northern portion of the volcanic area, and of the cossyrite trachytes broadly to the southern area supports Edwards (op. cit.) and Macdonald (1949) in their view of small cupola shaped chambers, forming more efficient differentiation cells than the larger magma chamber which supplied the basalts and trachyandesites, existing in localised areas of

volcanic provinces.

The non-vesicularity of the trachytes and comendites, and the lack of trachytic tuffs in the Nandewars, shows that the intrusion and minor extrusion of the trachytes was a relatively quiet process. It further shows that the volatile pressure in the cupola-like magma chambers was not very great. If volatile pressure had been great, volatile streaming (Edwards, 1935) would have given alkali enriched, perhaps phonolitic trachytes.

All the mineralogical evidence (the felspars and clinopyroxenes in particular) and the chemical evidence point to the development of the Nandewar alkaline series by processes of crystal fractionation. The normative salic constituents of the differentiated trachytes and comendites trend towards to the silica saturated minimum in the residua system $NaAlSiO_4$-$KAlSiO_4$-SiO_2 (Bowen, 1937b). All documented cases of volcanic provinces where the processes of crystal fractionation have operated show that the salic constituents of the residual liquids migrate to the low temperature trough of the residua system: the Otago province (Benson, 1941); Morotu (Yagi, 1953); Mauritius (Walker and Nicolaysen, 1954); Black Jack teschenites (Wilkinson, 1958); Gough Island (Le Maitre, 1962), and many other provinces.

Carmichael (1963) is of the opinion that in rock series where contamination has been an important factor (in the calc-alkaline series) the bulk normative felspar components of the rocks will plot in the two felspar field in the An-Ab-Or system. None of the plotted points in the Nandewar alkaline series (Fig. 8) enter this field, most of the normative felspar compositions actually defining the limit of the field of solid solution (Tuttle and Bowen, 1958). Hence any contamination which has occurred in the Nandewars

is minor. The continuous nature of the chemical trends, and the absence of xenocrysts and xenoliths of foreign material in the lavas, and the progressive nature of the variation of the felspars and clinopyroxenes, further supports the view of little or no contamination.

Age of the volcanism:

Solomon (1964) has made a study of the Mount Warning Shield Volcano from a geomorphological viewpoint. The volcano is very similar to the Nandewar volcano, and it is situated in the Eastern Australian region, on the N.S.W. - Queensland border near the coast. It consists of an eroded shield now forming an erosion caldera, with central trachytic plugs now evident in the eroded central area (Mount Warning, Mount Barney and Mount Alford complexes). Furthermore, the volcanic shield lies over a Mesozoic-Palaeozoic sedimentary contact. Solomon concludes (op. cit., p. 11) that the volcano is late Tertiary in age, perhaps Pliocene. The Nandewar shield volcano is very similar geomorphologically, and in the absence of any direct dating evidence, a roughly similar age is postulated for the Nandewars - late Tertiary, or perhaps earlier. The Mount Warning Shield Volcano is at present in a much wetter climate than the Nandewars, and it is to be expected that erosion would be more rapid than in the Nandewars. Broad contemporaneity between the two provinces can be assumed.

It appears that widespread tensional tectonic movements occurred in the Mid- to Late-Tertiary in Eastern Australia, and that volcanic activity has occurred at any place where sufficient crustal weakness existed. Erosion of the uplifted Permian orogenic belt in the New England area would produce isostatic readjustments (Voisey, 1959a) and flexing and movement along the margin of this belt, as in the Nandewar Mountain region, and also

near Mount Warning. These tectonic conditions are those shown by Tilley (1958) to be favourable to the development of alkaline volcanic activity.

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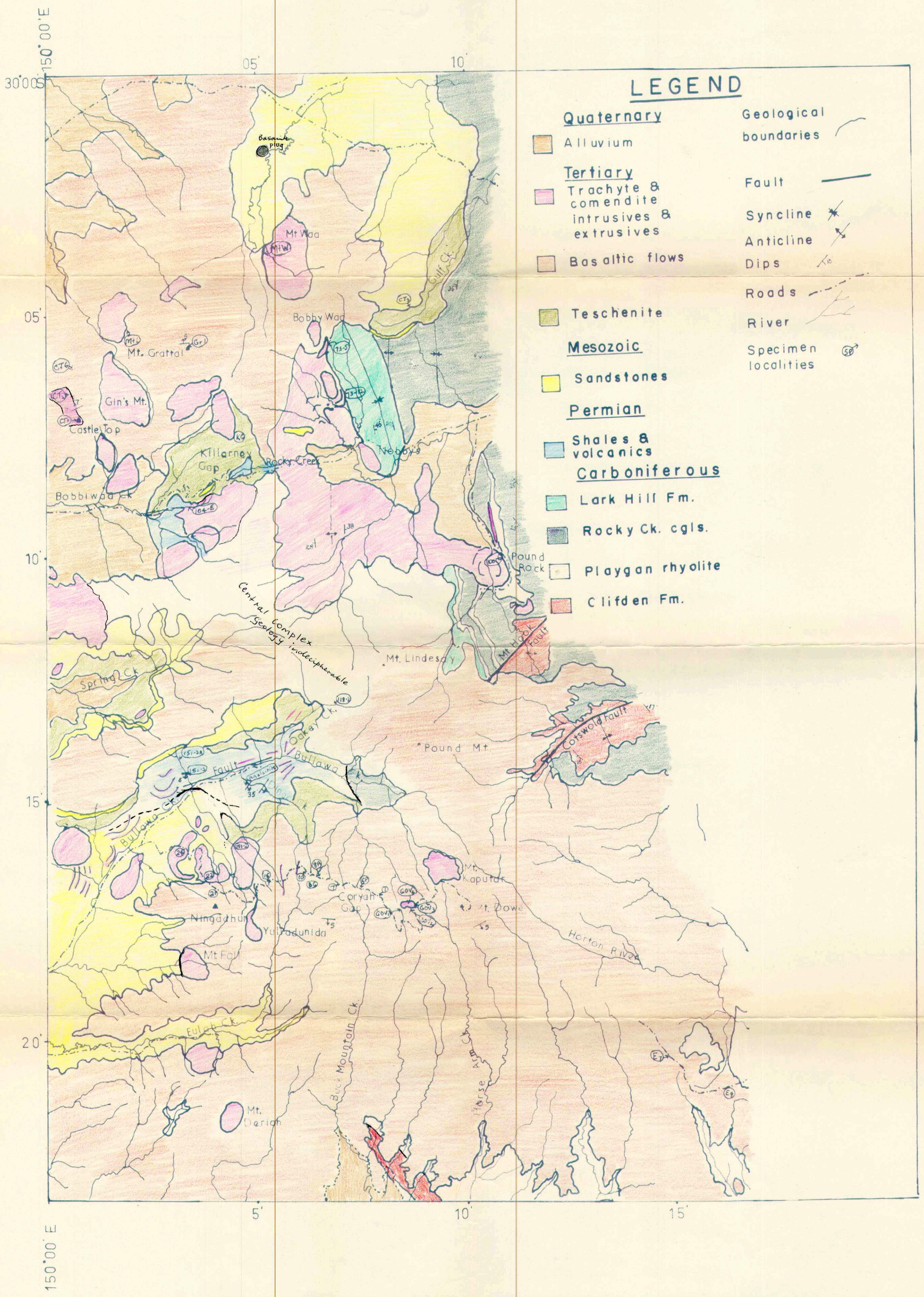
GEOLOGY OF THE NANDEWARS



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